

THE REAL ENVIRONMENTAL CRISIS  
– EFFECTS IN TOURISM DEVELOPMENT,  
CONFLICTS AND SUSTAINABILITY

Proceedings of the ASERS First on-line Conference on

*The Real Environmental Crisis – Effects in Tourism Development,  
Conflicts and Sustainability*



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The First Online International Conference on  
"The Real Environmental Crisis – Effects in Tourism Development, Conflicts and Sustainability"

**CRITICAL SUCCESS FACTORS OF ISO14001 EMS: WHAT  
RESEARCHERS MUST DO**

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**Abstract:**

*An environmental management system (EMS) provides the framework for continual environmental improvement through effective management of an organization's environmental impacts. The most well-known and accepted EMS is the ISO 14001 standard on environmental management established by the International Organization for Standardization (ISO). The key components that impact on EMS implementation are a synergistic blend of 'hard' and 'soft' elements. The elements of soft EMS are essentially dimensions of human resource management (HRM), while the 'hard' elements are more technical-oriented. To ensure successful environmental management, the 'hard' elements of an EMS must be accompanied by equal attention to the 'soft' elements. Despite of the growing interest in the voluntary environmental management standards, little empirical information exists on the critical success factors of environmental management (i.e. EMS implementation). Indeed more broad empirical studies and large sample surveys methodologies will be required for exploring the relationship of specific environmental management practices to environmental performance. Such empirically validated measurement instruments are essential to undertaking the development and testing of predictive theories of environmental management. In particular more effort should be placed in formulating theoretical models that can represent the complex EMS practices-environmental performance relationships. At the present time, the nature of the relationship between the soft elements, hard elements and environmental performance remains unclear. This paper aims to provide a motivation for investigating the link between the soft and hard elements to environmental performance.*

**Keywords:** ISO 14001 EMS, soft elements, hard elements, environmental performance.

**1. Introduction**

The ISO 14001 standard provides the guidelines for constructing an environmental management system (EMS) which has been designed to help organizations in the creation of structured mechanisms for continuous improvement in environmental performance (Kitazawa, and Sarkis 2000). Statistics published by the International Organization for Standardization (ISO) shows that up to the end of December 2008, at least 188 815 ISO 14001: 2004 certificates had been issued in 155 countries and economies. The 2008 total represents an increase of 34 243 (+ 22%) over 2007, when the total was 154 572 in 148 countries and economies (source: <http://www.iso.org>). Yet, despite of the growing widespread adoption of the voluntary environmental standard, little empirical information exists on the critical success factors of environmental management (i.e. ISO14001 EMS implementation). There is a need for a reliable and valid instrument grounded in a theoretical framework, which assesses specific environmental management practices to environmental performance at the organizational level. Essentially the key components that impact on ISO 14001 EMS implementation are a synergistic blend of 'hard' and 'soft' elements. The 'soft' elements are dimensions of human resource management (HRM), while the 'hard' elements are more technical-oriented. At the present time, the nature of the relationship between the soft elements, hard elements and environmental performance remains unclear. Hence this paper aims to provide a motivation for investigating the link between these three elements.

## 2. Theoretical Base of the Study: Natural Resource Based View of the firm (NRBV)

The resource-based view (RBV) proposes that sustained competitive advantage derives from the resources and capabilities a firm controls which must meet four conditions, namely, value, rareness, inimitability, and non-substitutability (Barney 1991). In general resources can be classified into three distinct categories: tangible resources, intangible resources and capabilities. Tangible resources include those factors containing an accounting value as recorded in the firm's balance sheet. Tangible resources are the physical and financial assets an organization possesses such as facilities, equipment, raw materials, other capital goods and stocks, etc. Intangible resources, on the other hand, include those factors that are non-physical (or non-financial) in nature and are rarely, if at all, included in the firm's balance sheet.

Intangible resources are items such as skills, knowledge, perceptions, processes, organizational culture, firm's reputation, human resource management policies, organizational structure, human capital etc. (Bansal 2005, Galbreath, and Galvin 2004, Carmeli, and Tishler 2004). According to Grant, capabilities encompasses the skills of individuals or groups as well as the organizational routines and interactions through which all the firm's resources are coordinated (cited in Fahy 2000, 98). In sum capabilities include organizational communication, employee know-how, managerial know-how, ability to build and maintain advantageous external relationships etc. (Carmeli, and Tishler 2004, Galbreath, and Galvin 2004).

Several researchers regard environmental protection as a source of competitive advantage (Madu 2004, Pil, and Rothenberg 2003, Thome and Smith 2000, Klassen, and Whybark 1999, Hart 1995). Building upon the RBV, Hart (1995) incorporated the constraints imposed and opportunities offered by the natural environment to develop the natural-resource-based view of the firm (NRBV). Resource-based rationales apply well to proactive environmental strategies such as the ISO 14001 EMS implementation for several reasons: (1) the implementation of proactive environmental strategies have been shown to affect environmental performance (Ann *et al.* 2006, Daily *et al.* 2003 2007, Montabon *et al.* 2000, Klassen, and Whybark 1999; Russo, and Fouts 1997); (2) corporate sustainable development requires investments of financial and/or human resources (Sharma, and Vredenburg 1998); (3) findings have shown that early adopters' ISO 14001 certification decisions are influenced by their prior internal capabilities, namely, pollution prevention competence and experience in continual improvement (Darnall 2003); (4) new resource-based opportunities from corporate sustainable development are created through changes in technology, legislation, and market forces (Porter, and van der Linde 1995); (5) findings have shown that successful implementation of environmental best practices and cost advantage results from the possession of complementary assets of process innovation and implementation (Christmann 2000). Complementary assets according to Teece (1986 cited in Christmann 2000, 664) are resources or capabilities that allow firms to capture the profits associated with a strategy, technology or innovation.

Findings have shown that ISO 14001 EMS implementation does produce value, through a variety of benefits which include: improved corporate image; environmental improvements; improved relations with communities; improved procedures; improved relations with authorities etc. (see for example Radonjic, and Tominc 2007, Radonjic, and Tominc 2006, Ann *et al.* 2006, Tan 2005, Poksinska *et al.* 2003, Corbett *et al.* 2003, Pan 2003, Montabon *et al.* 2000). For example, recent findings from a survey of Slovene manufacturing companies showed that certified enterprises consider ISO14001 as a very useful tool in promoting and adopting new cleaner technologies, and furthermore encouraged the development of environmentally conscious products (Radonjic, and Tominc 2006). In another study, Radonjic, and Tominc (2007) findings indicate that besides improving environmental performance, the ISO 14001 EMS influenced firms' economic performance through increased productivity. Again ISO14001 certification was shown to accelerate initiatives for

the adoption of new and cleaner technologies within certified firms in the Slovene manufacturing industry.

Despite ISO 14001 apparent widespread dissemination, there are powerful reasons to believe ISO 14001 program is imperfectly imitable for several reasons: (1) ISO 14001 is not a performance standard, it is a process based standard (Bansal, and Hunter 2003, Montabon *et al.* 2000); (2) ISO 14001 adopts the systems approach which applies not only to a specific area of the organization, but involves the coordination of various departments (Bansal, and Hunter 2003), and (3) Hart (1995) explained that the tacit nature of people intensive environmental capabilities makes them difficult to observe in practice and therefore hard to imitate.

Fernandez *et al.* (2003) emphasized that the weakness of organizations business culture and their shortcomings in human resources may be important impediments in the process of environmental action. Barney (1986) described organizational culture as valuable, rare and imperfectly imitable: thus, it has high potential for creating sustainable advantage. Adopting ISO14001 necessitates cultural changes, the core elements of which are embodied by the TQM principles (Kitazawa, and Sarkis 2000). In fact Strachan (1997) suggests that the systems of management recommended by BS7750, EMAS and ISO 14001 must be revised and stress on mechanistic solutions should be replaced with more participatory forms of management. As companies shift to more open forms of participative management, they begin the process of empowering their employees (Mallak, and Kurstedt 1996). Human resource management (HRM) has an important influence on the development of organizational capabilities and on firms' performance (Saa-Perez, and Garcia-Falcon 2002).

The 'soft' model of HRM as epitomized by the writings of Guest (1987) places emphasis on treating employees as a valuable asset, who, through their commitment, can provide improved performance. In essence soft HRM is seen necessarily to involve a focus upon fostering employee motivation, commitment and development (Legge 1995 cited in Kane *et al.* 1999, 496). Embarking on ISO 14001 EMS requires a broad spectrum of support from the organization and a strong internal commitment from its employees. The environmental management literature suggests that successful ISO14001 implementation and hence improved environmental performance can be accomplished through the use of 'appropriate HRM practices' (see for example, Kaur 2010, Daily *et al.* 2003, 2007, Govindarajulu, and Daily 2004, Daily, and Huang 2001).

Environmental investment can be grouped into three categories: 1) pollution prevention technologies, which are structural investments that reduce or eliminate pollution at the source, 2) pollution control technologies also referred as end-of-pipe technologies, are also structural investments that ensure a proper disposal of waste, reduce the release of pollutants, or correct past environmental damages, and 3) management systems which are infrastructural investments that improve environmental performance (Vachon 2007). Klassen, and Whybark's (1999) empirical findings showed firms significantly improved their manufacturing and environmental performance when a higher proportion of investment was allocated toward pollution prevention technologies. ISO 14001 guidelines' strong emphasis on pollution prevention can save companies money by improving efficiency and reducing costs of energy, materials, fines and penalties (Rondinelli, and Vastag 2000). Pollution prevention essentially entails preventing the creation of pollution and wastes through significant changes in existing production processes and requires a basic rethinking of product design (Bansal, and Hunter 2003, Christmann 2000, Klassen 2000, Hart 1995). Hart (1995, 1000) however described pollution prevention as 'people intensive, rather than technology intensive'. Moreover Bansal (2005) emphasized that pollution prevention requires employee involvement and empowerment. In sum Russo, and Fouts (1997) emphasized that pollution prevention stimulates firms to develop superior resources and capabilities more so than pollution control processes.



In light of the preceding discussion, one may conjecture that the tangible, intangible, and organizational aspects of environmental management systems can have a significant effect on ISO14001 EMS implementation and hence on the environmental performance. Thus the Resource-based rationales apply well to proactive environmental strategies such as the ISO 14001 EMS implementation.

### 3. Literature review

Several researchers suggest that the total quality management (TQM) elements should be incorporated in the organizations culture to ensure successful environmental management (see for example, Hart 1995, Klassen, and McLaughlin 1993, Kitazawa, and Sarkis, 2000). Essentially the elements of quality management practices can be grouped into two dimensions: 'infrastructure' and 'core quality management elements' (Flynn *et al.* 1995); 'soft' and 'hard' elements (Lam 1995, Lam 1996, Wilkinson 1992, Rahman, and Bullock 2005, Lewis *et al.* 2006, Ho *et al.* 2001, Samson, and Terziovski 1999, Thiagarajan, and Zairi 1997, Powell 1995). The infrastructure elements pertain to behavioral attributes of quality management, whereas the core elements relate to the technical aspects (Naor *et al.* 2008). The core quality management practices are expected to contribute to quality performance directly. Whereas the quality management infrastructure practices are proposed to support and facilitate the effective use of core quality management practices (Flynn *et al.* 1995). According to Lewis *et al.* (2006, 551) 'soft' elements are those intangible and difficult to be measured, while 'hard' elements are more systems-oriented. The elements of soft TQM according to Rahman, and Bullock (2005, 74) are essentially dimensions of human resource management (HRM). In general the 'soft TQM' elements include top management leadership, employee involvement, employee empowerment, employee training, teamwork and communication, strategic quality management, customer focus, workforce commitment, supplier relationship and shared vision. Whereas elements of 'hard TQM' include the use of advanced manufacturing systems, JIT principles, process management, quality data and reporting, design quality management, SPC usage, benchmarking, zero defect mentality (see Rahman, and Bullock 2005, Rahman 2004).

According to Rahman (2004) the relationship between TQM factors and organizational performance can be classified into two forms: individual and group. The individual form investigates the impact of each element of TQM on performance separately whereas in the group form, elements of TQM are grouped as 'soft TQM' and 'hard TQM' first and then the impact of these groups on performance is investigated. The literature provides empirical support for the significant contribution of soft elements of TQM towards various organizational performance measures. For example, Powell's (1995) empirical study in the US suggests that the key to TQM performance relies not in TQM tools and techniques such as ISO 9000 certification and benchmarking, but in 'intangible factors' such as employee empowerment, open culture and senior management commitment. Powell (1995, 15) concluded that 'organizations that acquire elements of soft TQM can outperform competitors with or without the accompanying TQM ideology'. Using a large sample of Australian and New Zealand manufacturing companies, Samson, and Terziovski (1999) showed by means of an empirical analysis that the 'softer' elements of TQM, i.e. leadership, people management and customer focus were the strongest predictors of operational performance, and the more systems and analytic oriented criteria (information and analysis, strategic quality planning, process management) did not. In Malaysia, Lau, and Idris (2001) examined the influence of soft TQM elements on various performance measures (growth, profitability, quality, market competitiveness). The authors concluded that culture, trust and teamwork were most influential in bringing about changes in the performance measures. The findings suggest that the key to performance lies in the softer elements of TQM. In a longitudinal study in the UK, Taylor, and Wright (2003) showed that senior management commitment in the TQM process significantly affected performance outcomes.

On the contrary, Rahman, and Bullock's (2005) empirical analysis of 261 Australian manufacturing companies provides evidence that certain hard TQM elements have a significant effect on performance and suggests that for hard TQM to impact performance, it is essential that such hard elements are supported by the elements of soft TQM. The simple regression analysis was used to examine the direct impact of: 1) soft TQM elements on performance, 2) hard TQM on performance and 3) relationship between soft TQM and hard TQM. Whereas the hierarchical regression was used to evaluate indirect effect of soft TQM on organizational performance through its effect on hard TQM elements. Rahman, and Bullock emphasized that organizations must have appropriate soft TQM elements in place to create conditions that allow effective diffusion and utilization of hard TQM elements. In another study, Ho *et al.* (2001) examined the link between supportive and core TQM practices and their impact on quality performance using a sample of 25 electronics companies in Hong Kong. The authors used the mean rating of all items within a subscale to create an index that reflects the extent to which that particular dimension of quality management practices has been implemented. The hierarchical regression was used to evaluate indirect effects of soft TQM on organizational performance through its effect on hard TQM elements. The results suggest that core TQM practices mediate the effect of supportive TQM practices on quality performance when the practices are taken as two integrated factors (i.e. group form). In particular the findings suggest that a complete mediation model appears to be a better representation of TQM practices-performance relationships than a partial mediation model.

At present, there are only a few studies in the existing literature on the critical factors contributing to successful ISO14001 EMS implementation. For example, Sambasivan, and Fei's (2008) empirical study of the electrical and electronics companies based in Malaysia identified the critical success factors for ISO14001 implementation. The choice of critical success factors were based on the five main clauses of ISO14001 and the external factors that motivate a company to implement EMS. The five main clauses of ISO14001 are: 1) environmental policy, 2) planning, 3) implementation and operation, 4) checking and corrective action, and 5) management review. The first factor, 'management approach', embraces three clauses: environmental policy, planning and management review. The second factor, 'organizational change', embraces the third clause, i.e. implementation and operation. The third factor, 'external and social aspects', deals with aspects such as government regulations, market pressure, and customer requirements that motivate an organization to adopt and implement ISO14001. The fourth factor, 'technical aspects', embraces the clause that deals with checking and corrective action. In particular the technical aspects of ISO14001 include: assistance from environmental specialists, availability of monitoring and measuring equipment, and the production process enhancement. The results of the analytic hierarchy process (AHP) indicate that the critical success factors in order of importance are: management approach, organizational change, technical aspects, and external and social aspects that influence the implementation of ISO14001.

Employing a sample of 36 Indian ISO14001 certified companies Padma *et al.* (2008) study's objectives were threefold: 1) to identify the critical factors (CFs) of ISO14000, 2) determine if ISO14000 certification results in improved organizational performance, and 3) to analyze the levels of and changes in the CFs and organizational performance (IOPs) due to certification. The critical factors consist of: 1) top management commitment, 2) environmental issues identification and legal compliance, 3) environmental process management, 4) emergency preparedness and response, 5) continuous improvement, 6) measurement, monitoring and control and 7) human resource management. The indicators of organizational performance (IOPs) include: 1) customer satisfaction, 2) employee morale, 3) growth in exports, 4) profitability, 5) overall productivity, 6) reduction in quality costs, 7) overall financial performance, 8) overall operational performance, and 9) savings in energy and environmentally desirable impact of product/service. The findings indicate that firms'

regard the preparation for emergencies as an integral part of environmental management systems (EMS), and they seem to initially struggle to identify environmental issues that are to be given higher importance. Furthermore, the certified firms find it difficult to continuously improve their environmental management processes. Findings indicate significant changes in all the CFs and IOPs due to ISO 14.000 certification. Furthermore, more experienced firms have higher mean values for all the CFs in comparison with less-experienced firms.

Wee, and Quazi's (2005) empirical analysis of 151 Singaporean electronics and chemical manufacturing companies identified and validated seven critical success elements of environmental management which include: top management commitment, total involvement of employees, training, green product/design, supplier management, measurement and information management. The authors however, did not test the relationship between the critical success factors with environmental performance.

Govindarajulu, and Daily's (2004, 365) theoretical framework provides practitioners valuable information for developing plans to inspire and retain employee motivation for environmental improvement efforts in organizations. The framework emphasizes the integration of management commitment, employee empowerment, feedback and review, and rewards as key elements for successful implementation of an ISO14001 EMS and hence enhanced environmental performance. Adopting the framework, Kaur (2010) ascertained the hypothesized relationships. Her study was conducted in five manufacturing companies currently certified to ISO 14001 EMS. Moreover four of these companies are recipients of the Malaysian Prime Minister's Hibiscus Award (PMHA), Malaysia's premier private sector environmental award for business and industry. The empirical findings suggest that management commitment, empowerment, and feedback and review have a significant positive relationship to perceived environmental performance. However, the link between rewards and perceived environmental performance was negative but statistically insignificant.

Daily, and Huang (2001) proposed a conceptual model of the EMS-HR factors to assist in proper facilitation of the environmental management program. The model identifies human resource (HR) factors such as top management support, environmental training, employee empowerment, teamwork and rewards systems as key elements of the implementation process of an EMS. Recently Daily *et al.* (2003, 2007) studied the impact of human resource (HR) factors on 437 employees' perception of environmental performance in a facility currently certified to ISO 14001. The findings suggest that management support, training, employee empowerment, and rewards are related to perceived environmental performance. Moreover, teamwork played an important mediating role between some of the HR factors and perceived environmental performance.

Zutshi, and Sohal (2004) presented the critical success factors for successful implementation and maintenance of environmental management systems (EMS). The initial research was undertaken using a three-phase approach: a questionnaire survey mailed to 286 Australasian organizations certified with ISO14001 and interviews (nine preliminary interviews and 12 in-depth interviews) conducted with managers responsible for various management systems, primarily environmental, quality and occupational health and safety. The critical success factors are presented under four broad headings, namely: management leadership and support, learning and training, internal analysis and sustainability. The first factor, 'management leadership and support' deals with aspects such as top management commitment, cultural change and organizational vision, allocation of resources, appointment of a champion, importance of communication and avoidance of personality clashes. The second factor, 'learning and training' includes: learning from other organizations experiences and benchmarking, reference to industry guidelines/standards, employee induction and training, general training and awareness for suppliers and other stakeholders.

The third factor, 'internal analysis' includes: conducting cost-benefit analysis, Initial Environmental Review, IER / gap analysis, identification of aspects and impacts and setting of



objectives and targets, necessity and usage of audits, document control systems, and integration of existing management systems. The fourth factor, ‘sustainability’, deals with aspects such as Life cycle analysis (LCA), design for disassembly (DfD) and industrial ecology.

Babakri *et al.* (2003) presented the results of an empirical study on 584 US industrial companies with the aim of identifying some of the critical factors for successful implementation of the ISO 14001 registration process. Out of the seventeen ISO 14001 elements, eight elements received high mean scores in the survey. The eight ISO standard’s elements requiring the greatest effort and time to implement are: identifying environmental aspects, environmental management systems (EMS) documentation, training, EMS audit, operational control, environmental management program, objectives and targets, and document control.

Kitazawa, and Sarkis (2000) case studies of the relationship between ISO 14001 EMS and the continuous source reduction programmes of three industrial companies identified employee empowerment, their willingness to make suggestions for improvement and management’s effort to create employee participation in decision making are three critical elements for successful continuous source reduction activities (i.e. reducing waste or toxicity of substances).

Chin *et al.* (1999) studied the critical success factors to implement ISO14001 based EMS to be considered by the Hong Kong manufacturing companies. The success factors for ISO14000 implementation are: management attitude, organizational change, external and social aspects, as well as technical aspects. The first factor, ‘management attitude’ deals with aspects such as top management commitment and support, appropriate environmental policy, and regular management reviews. The second factor, ‘organizational change’ includes: structure and responsibility, training and awareness, communication, documentation and control, and emergency preparedness. The third factor, ‘external and social aspects’, deals with aspects such as environmental legislation, market pressure and employee relations. The fourth factor, ‘technical aspects’ include: assistance from environmental specialists, availability of monitoring and measuring equipment, and the production process enhancement. The results of the analytic hierarchy process (AHP) indicate that the success factors in order of importance are: management attitude, external and social aspects, and organizational change. The findings however suggest that Hong Kong manufacturing companies did not into consideration the technical aspects in the implementation of ISO14001.

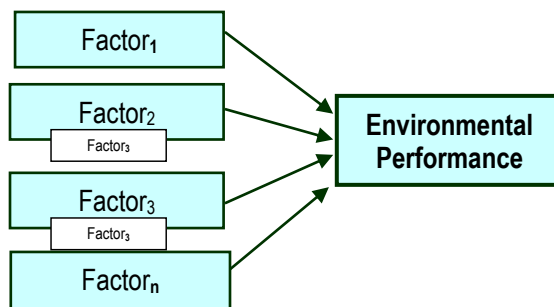
Quazi (1999) reports on the findings based on seven case studies conducted with companies which are either ISO14001 certified or in the process of certification in Singapore. His findings revealed that management commitment, consultants, availability of resources, employee cooperation, ISO9000 certification, strong quality culture, and communication are critical success factors (CSFs). Other CFSs identified in the literature review were not uniformly applicable to these companies. The majority of the sample (57 percent) identified management commitment as one of the CSF during the implementation of EMS. Moreover about 30 percent of these companies identified employee cooperation as a CSF. Two companies were in the process of implementing EMS, and hence were not able to identify such factors at the time of interview.

In summary the literature on quality management, a similar endeavour to environmental management suggests that the key components that have impact on ISO14001 EMS implementation are a synergistic blend of ‘hard’ and ‘soft’ elements. The soft elements are essentially dimensions of human resource management (HRM), while the hard elements are more technical-oriented. Specifically the soft elements are essential for supporting and facilitating effective utilization of the hard elements (Rahman, and Bullock 2005, Ho *et al.* 2001, Flynn *et al.* 1995). Furthermore, many of the studies reviewed in the preceding discussion did not test the relationship between the critical success factors with environmental performance. Very often survey-based perceptual measures are used to assess environmental performance. Klassen, and McLaughlin (1996) acknowledged that because many different conceptualizations exists as to how researchers and/or practitioners might

operationally define the environmental performance construct, hence the difficulty of defining environmental performance and then operationalizing the construct as a measurable variable needs further attention.

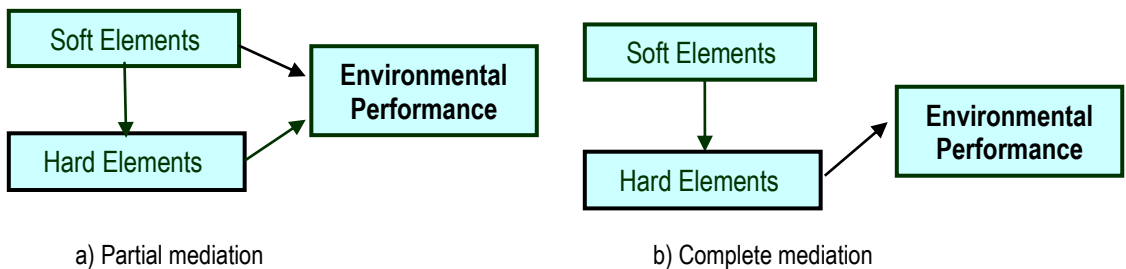
#### 4. Proposed theoretical framework for environmental performance

At the present time, the nature of the relationship between the soft elements, hard elements and environmental performance remains unclear. In light of the preceding discussions, it seems both theoretically and empirically plausible that the relationship between the soft elements, hard elements and environmental performance can be categorized at the individual and group form. As shown in Figure 1, the individual form investigates the impact of each elements of ISO14001 EMS on environmental performance separately. To date the studies that belong to this form are Daily *et al.* (2003, 2007), and Kaur (2010). These studies examined the impact of human resource (HR factors) on perceived environmental performance at the individual level of analysis.



**Figure 1.** Effect of elements of ISO14001 EMS on environmental performance as individual factors

In the group form (shown in figure 2), elements of ISO14001 EMS are grouped as 'soft elements' and 'hard elements' first and then the impact of these groups on environmental performance is investigated. As suggested by Ho *et al.* (2001) the mean rating of all items within a subscale can be calculated to estimate the extent to which that particular dimension of environmental management practices has been implemented. Future researchers can attempt to examine the mediation effects of hard elements in the relationship between soft elements and environmental performance. In order to explore the mediating role of hard elements, there are two possible kinds of relationships, i.e. partial and complete mediation. A complete mediation model specifies the relationship between soft elements (antecedent), hard elements (mediator) and environmental performance (consequence) in the form of soft elements → hard elements → environmental performance. The soft elements influence the environmental performance only indirectly through the hard elements. In other words, all the influence of soft elements on environmental performance is transmitted by hard elements. Apart from the effect of complete mediation, partial mediation would also exist. In a partial mediation model, soft elements have not only indirect influence on environmental performance through hard elements, but also direct influence on environmental performance. That is, only part of the total influence of soft elements on environmental performance is transmitted by hard elements. Perfect or complete mediation exists when the soft elements has no effect on the environmental performance when the hard elements is held constant.



**Figure 2.** Effects of ISO 14001 EMS elements on environmental performance as groups

## 5. Conclusion

Indeed more broad empirical studies and large sample surveys methodologies will be required for exploring the relationship of specific environmental management practices to environmental performance. Such empirically validated measurement instruments are essential to undertaking the development and testing of predictive theories of environmental management. In particular more effort should be placed in formulating theoretical models that can represent the complex ISO14001 EMS practices-environmental performance relationships. To aid potential research in this area, the following research propositions are proposed for empirical testing:

- P1: soft EMS elements have direct affects on environmental performance
- P2: hard EMS elements have direct affects on environmental performance
- P3: soft EMS elements have direct affects on environmental performance on the adoption and utilization of hard EMS elements
- P4: soft EMS elements indirectly affect environmental performance through its effect on hard EMS elements.

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# LEGAL REQUIREMENTS FOR THE ENVIRONMENT ACCORDING TO EUROPEAN CONVENTIONS Especially in South – Eastern Balkan countries

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## Abstract:

*This paper work pretends to testify the risks the environment has been facing with for decades in the global aspects and at the same time the reaction of the human society that by strong legal means to impact in the protection of this system. Now when the global social-economical development has shown an unforeseen growth before, we have silently ascertained that in parallel alongside with this progress the environment where we live has been degraded and destructed not thinking at all that the future generations have the right to live normally as well. The seventieth of XX Century indicate the intensification and mobilization of responsible governments for environment protection programs. Gradually this issue has moved to international instances and institutions which have issued series of declarations, directives, and conventions and they recommend and enforce governments of countries to approximate their national legislations with the principles and standards provided by these significant documents. In addition, due to the increase of high social risk and the dynamic of environment destruction, two other conventions have been issued which enforce countries to regulate their liability for environment protection with the Civil Law and Criminal Law, this way qualifying and considering the destructive activities of subjects towards the environment.*

**Keywords:** Legislation, environment, civil and criminal liability, convention, directive.

## 1. Introduction

The technical and technological development of the late years of the last century has created many dangerous centers for the environment. This condition has been caused by the human kind itself by misadministration not only of nature and its resources, but also the work environment and it has brought great damages to their lives, their physical integrity, health, wealth and other values. At the same time by such actions the basis of human survival is being seriously and extremely jeopardized. Due to the high rate this risk indicates, the international community has undertaken a series of measures, procedures and resources in order to eliminate, prevent, or minimize these threatening centers for the environment and for the human life itself.

It is undisputable that the risk for the destruction of environment equilibriums has become a global problem which threatens the entire global living environment. Starting from these concerns, the international community has started to reflect a more serious engagement in the prevention and protection plan in this field. Our country is also in the phase of social, economical, political and legislative reforms. In this aspect it is paying special attention to the issue of harmonization, respectively approximation of the local legislation with the regulations, acts and important international documents which aim for environment balance. In this sense, the aspect of environment protection and elimination of damages caused by possible centers of existing or potential risks is assessed as of special significance, which shows the urgent need to harmonize much deeper and with more diligence the legislative basis in conformity with both conventions: The Convention for Civil liability for the damages caused from dangerous activities for the environment from 1993, and the Convention on the protection of living environment through the criminal Law in year 1998. Moreover, due to the importance the environment protection has now, there are several documents and recommendations which enforce countries to act on the legislative, economical, and social, and

lately the humanitarian aspects. The aim of these elements is the composition of the legislative basis and economical measures which always must be developed upon sustainable bases towards environment protection.

## 2. Civil Liability

In accordance with the Rio Declaration on the Environment of year 1992<sup>1</sup>, in order to regulate and provide a due compensation for eventual damages caused by dangerous activities for the environment, the European Commission issued the Convention on the civil liability of subjects performing dangerous activities for the environment on 21 June 1993, in Lugano.<sup>2</sup> The entrance dispositions of this Convention have created clear essential concepts so that their content will be interpreted similarly by each member of this old European organization. In the environment and the liability aspect, this Convention considers of great significance: the life resources as abiotic and biotic, air, water, earth, flora, fauna, and other elements in interaction between these factors. The said Convention tends to regulate the specific environment protection which could be exposed or effected by different dangerous resources. In addition, property aspects are also regulated, especially those being a part of cultural inheritance, and special aspects of landscapes.<sup>3</sup>

According to the dispositions of this Convention the following would be considered as dangerous: production, treating, storage, use, or emission of one or more dangerous substances, or any activities which is of the similar nature relating these substances, production, agricultural, treating, storage, use, destruction, disposal, emission, or any other activities of one or more genetically modified organisms or micro-organisms which represent significant danger for the human kind, environment, or property, work and setting of cremation equipments, treatment, or recycling of solid waste, with the condition that these represent a significant danger for the human kind and the environment.<sup>4</sup>

When interpreting the said convention it is stressed how a substance or hazardous substances prepared in advance have the ability to emit a hazard for the environment and the human kind, and their property (e.g. explosive, oxidative, carbonating, toxic, hazardous, corrosive, irritating devices, etc.) raise the liability for the eventual dispute or contractual damage, which has to be compensated if it is done. The incidents towards causing environment damage could be any unexpected continuous phenomenon or events which are of the same origin, causing damages ore raise permanent serious risks to cause damage. Due to the effects of dangerous activities, damaged substances or products endangers or could endanger the environment condition, which manifests in the emergence of particular damages. Damages caused from a particular subject which have to be compensated in conformity with the foreseen regulations of the convention are: dying or personal injury, loss or damage of property in the aspect of dangerous activities, loss or damage on the environment, costs of prevention measures and any damages caused by the execution of these measures. The eventual liability for the caused damages is clearly regulated by the dispositions of the European Convention, and if this damage has been caused after the entry into force of this international legal act, or if the incident has happened in the territory of a contractual party, regardless where the damage consequences occur, it is always the subjects that are charged with the liability. This liability could be carried in two forms as following: the Liability regarding particular

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<sup>1</sup> Rio Declaration on Environment and Development, Having met at Rio de Janeiro from 3 to 14 June 1992, për shumë shih ne <http://www.unep.org/Documents.Multilingual/Default.asp?documentid=78&articleid=1163>.

<sup>2</sup> Convention on Civil Liability for Damage Resulting from Activities Dangerous to the Environment Lugano, 21.VI.1993, për më shumë shih ne <http://conventions.coe.int/treaty/en/treaties/html/150.htm>.

<sup>3</sup> Herewith

<sup>4</sup> herewith

substances, organisms and settings of solid waste or places; and the Liability of a permanent place for waste extermination.

In the first case, the carrier of substances who performs a dangerous activity is liable for the caused damage because the operation with such substances has been the result of the accident, or during the period he has the activities on control. In other cases the carrier, respectively the operator is liable for continuous regularity of waste deposit and if during this time a damage is done during their deposit on that place raises the civil liability alongside with obligation to compensate the damage. From the regulations on the liability for caused damages the convention has foreseen some exceptions in cases when the operator is free of obligation. These cases are when the damage is caused in events of hostility, civil war, natural phenomenon of extraordinary nature which neither can be avoided nor can they object the activities of a third party, or acceptable levels of pollution ( and what are the acceptable levels of pollutions is a factual issue which has to be solved for each case considering all the circumstances of the objective or subjective aspect), or the dangerous activities which have been performed in compliance with the law on the interest of a person who has been damaged.

The liability for the damage caused from pollution has been practically reduced to a compensation only for material and immaterial damage. The request for compensation is initiated to the national court authorities and at the place where the loss has been caused, or at the place where dangerous activities has been performed, or on the basis of permanent inhabitation of the sued party (the so-called alternative jurisdiction). However, this convention gives the possibility for the requirements of particular subjects, bodies and organizations dealing with protection, preservation and improvement of environment to be given a quality civil-legal protection. Therefore with this legal act it is managed to:

- ☞ Prohibit dangerous illegal activities which are a serious threat for environment damage,
- ☞ Have operators on charge to undertake particular and exactly specified measures in order to prevent incidents or events of such damages in the future,
- ☞ Have operators in charge to undertake measures after the incident in order to prevent damages also in the future,
- ☞ Have operators on charge to undertake measures in order to turn back on the previous condition of damaged places or items.

In order to increase the liability of individuals, natural or legal persons, companies, institutions or other organizations of the multiethnic nature, this convention has enforced many countries and international organization to organize campaigns in the field of reduction, preservation, promotion, and protection of the living environment in the international frames. However, it was soon ascertained that for such an efficient social-legal reaction it was not sufficient only the possibility of creating civil liabilities for damages caused in the environment. After five years of intensive efforts of many scientists and experts it was managed to adopt the new European Convention, which sets a significant basis and the framework of criminal liability for such damages caused by the environment.

### 3. Criminal liability

For the first time in Southern Eastern Balkans a protection has been provided for the environment through criminal law, in accordance with the international Convention through Criminal Law<sup>5</sup>. Within the scope of this law, our country has respected the principles and requirements of the International Convention on the Protection of Environment through Criminal Law. This Convention

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<sup>5</sup> European Council, Committee on the Environment, Regional Planning and Local Authorities, Strasbourg, year 1998

has been adopted by the European Council in Strasbourg on 4<sup>th</sup> of November 1998<sup>6</sup>. Thereby this very important international act aimed to enhance efficiency and quality of the plan on environment protection in the region and tasks that serve to classify actions or offences committed by certain entities against the environment as punishable offences when such actions have caused damages or serious harm on the environment. Practically, such solutions managed to establish effective unique grounds for criminal – legal protection of environment within the European territory and unify basic responsibilities of natural legal persons for any eventual commission of these criminal offences<sup>7</sup>. It has to be taken into account that the noted convention, in the environment protection plan, recommends to issue and adopt other legal acts that are outside the scope of the criminal law and cause harm to the environment (such as administrative offences etc), such offences also need to be punishable and regulated with an appropriate legislation.

All the countries that have signed this Convention are required to undertake actions and certain activities. These activities are of the dubious character: national and international level. Within the national level this convention establishes the foundation to anticipate certain behaviours, criminal offences and description of criminal sanctions against the perpetrators within the criminal legislation. Within the international level this reflects commitment and perfection of the rules in legal-international cooperation amongst the countries against the criminal activities that might harm the environment in the region and wider.

The provisions set forth in this Convention, specifically under the Section 2, stipulate the object of environment protection. Certain objects are considered: humans or certain values of human life, physical and health integrity, air, water, soil, protected monuments, other protected facilities, property, plants and animals. As forms of threats to these protected values special actions have been determined (an action or inaction failure) that are associated with certain substances that cause ionizing radiation, hazardous waste, hazardous activities, nuclear material and other dangerous radioactive materials that threaten the environment or its individual components. These activities may be committed intentionally or by gross negligence. In Europe, in the viewpoint of criminal law and its harmonization with environment protection it is particularly important to clearly define ways and forms to handle with hazardous activities.

Commission of certain offences such as criminal offences that infringe, restrict or endanger the environment in accordance with the provisions of this Convention for criminal conviction are set by the following activities:

- ☞ the discharge, emission or introduction of a quantity of substances or ionizing radiation into air, soil or water which
- ☞ the unlawful disposal, treatment, storage, transport, export or import of hazardous waste

The unlawful operation of a plant where a dangerous activity is carried out and which causes or is likely to cause death or serious injury to any persons or substantial damage to protected monuments, other protected objects, property, animals or plants;

Apart from these actions and activities classified as criminal offences that intent or assist to carry out activities that violate and threaten the environment it is foreseen to punish appropriately. This clearly means that the provisions set forth under the Convention foresee responsibilities in the form of cooperation in encouraging and supporting the struggle towards prevention and repression against the criminal offences of this nature. For these prohibited and illegal offences and activities

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<sup>6</sup> Convention on the Protection of Environment through Criminal Law CETS No. 172 for more please see <http://conventions.coe.int/treaty/Commun/QueVoulezVous.asp?NT=172&CL=ENG>

<sup>7</sup> Criminal Code of Kosovo, Chapter XXIV, due to the environment importance, animals, plants and cultural objects, in accordance with the Convention on the Protection of Environment through Criminal Law has provided legal-criminal protection to certain offences that in this way jeopardizes social life.

committed by natural and legal persons, the convention provides certain types of measures and criminal sanctions. These sanctions are different such as: punishment by imprisonment and property seizure (in the form of assets, incomes or other assets).

Despite fines and liabilities that sanction a criminal offence, there are other punishable measures that serve to maintain a sustainable and balanced environment within the scope of secondary legislation. This Convention does not imply a direct application in special environment cases. Provisions are to be applied only if countries are individually determined to do so. This means that the European Council and others that recognize and implement this convention unilaterally are required to include this in their national criminal legislation, including the penalty system by providing them in accordance to their type and according to the level of penalty in compliance with the convention framework.

#### 4. Environmental legislation

The concept for appropriate and modern legislation for a healthy environment means that it is a task of each and everyone to have an ultimate goal for economic development in accordance with sustainability principles. If we look in the formal-legal aspect, knowing the relevance of the environment and the complexity that it contains for the society, apart from the internal legal framework, initially it requires having the role and power of the international legislation. Within this plan it requires starting by assessing the Stockholm Declaration on the Human Environment dated on 1972<sup>8</sup>. This declaration has been adopted aiming to set up the foundation of a equilibrated ecological development which explicitly aims to deduct the risk in the sense of provision of conditions that impact on life and its qualities by paying special attention to environment protection. Apart from Stockholm Declaration, the United Nations made a decision to establish competent central bodies not only to handle with the problem of environment protection, but also with the coordination of activities in this area- UNEP Program (*United Nations Environment Program*)<sup>9</sup>, which operates since 1973. The importance of Stockholm conference about the right to live in a healthy and suitable environment was a solid ground of many international reports and a basic important legal act for many national constitutions and court rulings. With the aim to accomplish the international legislation for the regulation of mutual issues, being well aware of the problem of an effective and efficient control of trans-border movements of toxic waste, the Basel Convention has been adopted in 1992. The aim of this convention and its protocols is to ensure a completed legislative framework in order to perform a full control of the trans-border movement of dangerous material and toxic waste. Additionally, this document within its provisions regulates the responsibilities and duly payments of compensations for the damages caused as a result of the trans-border movements of dangerous substances and toxic waste, including even the incidents that might occur as a consequence of illegal trafficking.

In order to provide a more efficient legal basis and a rational reaction worldwide, the United Nations Conference for Environment and Development was held in Rio de Janeiro, in 1992.. In the summit which was organized on the highest level took part 178 countries and the majority voted for the United Nation Declaration for Environment and Sustainable Development which contains 27 principles stipulated in terms for sustainable development.<sup>10</sup> In this summit the principles of the Stockholm Declarations are still being elaborated and a new perception is being introduced that the obligation and the way of environment protection is not only of the national category but also a universal one. The commission for Sustainable Development was established as a body of the United Nations with the clear task to monitor the further course of actions started at the Earth

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<sup>8</sup> <http://www.unep.org/Documents.Multilingual/Default.asp?documentid=97&articleid=1503>

<sup>9</sup> For more in relation to the mission and program of this forum please see <http://www.unep.org>

<sup>10</sup> <http://www.unep.org/Documents.Multilingual/Default.asp?documentid=78&articleid=1163>



Summit in Rio. The Commission for Sustainable Development gathers each year in the United Nations and in specific sessions it is committed to a particular subject. In the conference in Rio de Janeiro a global action plan was adopted for sustainable development for XXI Century. The obligations that emerge from Agenda 21 enforce 173 recipient countries. Agenda 21 is of great significance for the local governing because it foresees and regulates a specific role for the local authorities in order to begin with the process of sustainable development in this level. In this universal act it is stressed that ‘... each local authority must enter into dialog with its citizens, local and private organizations, companies, etc. and to co-consent the local Agenda 21. Based on these dispositions, respectively international obligations, the government should create the legislative basis in order to reach a consensus with the wide local, civil public, particular social categories, commercial and industrial subjects, and to collect close and necessary information to compile initially a local legislative strategy, which at the end it should be appropriate in order to be integrated in both the national and international strategy. The Millennium Summit of the United Nations which dealt with the purposes for development and the schedules for the implementation of the stipulated principles for environment protection has set eight essential objectives. This was done in order to encourage all countries to participate in solving problems in the human development aspect. The objectives include 18 clear possible tasks to be achieved through: policies and programs in the country; international aid; and engagement of the civil society

Implementation of these objectives has to be achieved retroactively in a period of 25 years starting from 1990 until 2015. One of the eight main objectives on ensuring the environment protection has to be achieved by accomplishing three tasks:

- 1.integration of sustainable development principles into policies and programs of the country and by reversing the harmful process of natural resources on the other direction;
- 2.increase of people percentage by 2012 to have a sustainable access to drinking water, and
- 3.Achievement of a sound improvement of living condition of at least 100.000.000 inhabitants of poor neighbourhoods as of 2020<sup>11</sup>.

In this meeting a conclusion was achieved that many efforts for environment protection have shown no results and this mainly due to the largest world polluters (USA, Russia and others). They did not accept principles encompassed in previous declaration and conventions issued. The problems of climate change and global warming become a focus only when a harmful change occurs in our lives and when the social reaction is the only opportunity to improve such radical changes. The reaction of international community in the legal-formal plan towards this alarming situation has seriously started to be implemented based on Kyoto Treaty, a legal act that regulates the issue of environment protection from the polluting activities and what they impact on our climate. This proves that there has been a serious effort by eligible countries for their responsibilities undertaken in accordance with the Convention. The Kyoto Protocol has been adopted in Kyoto, Japan, on 11<sup>th</sup> of December 1997 and has entered into force on 16<sup>th</sup> of February 2005. Insofar, this was signed by more then 140 countries. The detailed rules on the implementation of the Protocol were approved in COP 7 in Marrakech in 2001, the so-called “Marrakech Agreement”.

The objective is to ensure stabilization and reconstruction of greenhouse gas concentrations in the atmosphere at a level that would prevent dangerous anthropogenic interference with the climate system. The objectives are clearly defined and simultaneously set up requirements to developing countries, countries with transitional economy and to industrialized countries to continuously apply this protocol. The protocol regulates, respectively the target agreed upon was an average reduction of 5.2% from 1990 in the period from 2008 until 2012. All the countries that are

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<sup>11</sup> World Summit on Sustainable Development held on 2002 in Johannesburg  
[http://www.un.org/jsummit/html/basic\\_info/basicinfo.html](http://www.un.org/jsummit/html/basic_info/basicinfo.html)

required to reduce gas emissions are listed in Annex 1 of the Kyoto Protocol. The European Union is one of the largest supporters of this Protocol. This important legal act has ratified with the decision of the Council of Ministers of the European Union. This entered into force on 31<sup>st</sup> of May 2002.

Negotiations on concluding a new agreement commenced during early 2008 that shall replace the Coyote Protocol. Based upon the agreement, UN Experts were authorized and designated to conduct assessments about the climate changes, aiming to restrict gas emissions in all the countries even though there happens to be serious disagreements on this issue in the sense of distributing the burden amongst the rich headed by United States, and developing countries such as China and India. As far as the developing countries are concerned, including Kosovo, Albania etc, the Protocol does not provide new requirements in connection with those foreseen by the Convention, i.e. there is no anticipation about the requirement for reduction of greenhouse emission, but it provides the possibility that each of them may take upon itself a responsibility based on its capability. In order to produce effects and create institutional conditions, it is necessary for the Protocol to undertake further actions such as: a register for gas emission; commitment of relevant state institutions to cooperate with UN bodies in charge to implement the Convention, and the noted Protocol. This requires to be implemented by establishing partnerships with interested investors aiming to use clean technology in the Republic of Kosovo and transfer of knowledge, including the necessary measures for a transparent process of investments that are financially attractive. Afterwards the activity and attention needs to be increased in relation to the issues for the definition and content of the environment protection, the right to live in a healthy environment i.e. procedural aspects of this legislation, which mean the procedural rights as follows: access to information in respect to the living environment, participation in decision-making in relation with the environment and the right to make questions for the decisions made with regard to environment, including the procedural rights for certain issues that need to be filed to the court. This procedural regulation of the noted issues is important because it establishes a flexible and affordable process for environment protection.

## 5. Voluntary activities

Voluntary activities mean actions undertaken by an individual or an organization aiming to protect the environment that are not regulated by the legislation nor motivated for any material benefit. Actually, voluntary activity is the essential mean based on which the majority of citizens aiming to change their life influence in the stability and sustainable development. Individuals may be engaged in various voluntary activities one of which could be the consumption on is the so-called "green", recycling process, ethical investments and voluntary work aiming to protect the environment.

Governments may and have to exercise influence on voluntary activities through different means and strategies of communication which could be in form of information campaigns, and which enable determination and identification of ecological benefits i.e. recycling of plastic bottles, newspapers, etc., thereby influencing in the awareness of citizens about their rights on maintaining a clean and protected environment. In addition, they need to be aware of their right to file charges to the relevant Court against entities that harm the environment. Officials have always the possibility to make decisions that impact on the awareness of others in respect to the needs for protection of ecology by reviewing possibilities through green actions to generate profit. Additionally, governments, apart from the legislative framework, they can actively undertake other actions that serve in fulfilling the ecological international standards<sup>12</sup>. The regulation of environment protection

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<sup>12</sup> In relation to ISO standards please see: <http://www.iso14000-iso14001-environmental-management.com/> ISO 14000, ISO14001 ISO 14004 the myriad of ISO14000 standards and information related to environmental

can be enhanced also through “memorandums of understanding” which means undertaking liability in voluntary manner by enterprises, organizations or business organizations based upon recommendations or agreements with the government, and in cases of violation to be subject of sanctions<sup>13</sup>.

Within the scope of ecology, MoUs have several essential advantages. They provide an action strategy that is very flexible in achieving protection purposes and due to the fact that entire provisions (example. manufacturers or service providers) provide selection of the best option in achieving their goals and they require few or no state institution interference. Voluntary memorandums of understanding may produce a constructive cooperation between state institutions and the industry dealing with the sphere of ecological modernization which consequently leads towards a change of perception for a new behaviour as a state, as well as the same shall apply for officials or manufacturers. However, it has to be taken into account that these agreements also constitute weaknesses. In practice they are usually too ambitious since they are related to issues that are irrelevant and their liabilities do not produce any essential effect. MoUs are not mechanisms that empower the law. The lack of sanctions within these MoUs may impact negatively in preserving the ecological resources.

## 6. Conclusion

Clearly, during the last century the awareness and perception of people and governments was positively provoked in respect to environment protection, in both national and international level. This concern can also be noticed within the governmental programs on protection of environment and sustainable development, which is deemed to one of the priority issues. There is no doubt that people need to preserve, promote and protect the environment. However, the damage caused insofar and the danger which is constantly present due to economic growth does not remain a limited problem in a territory of a single country. Therefore, it is logical for the international community to analyze these risks and to mobilize countries about this risk alarm from the environment pollution on a global level, as well as the need for the proper quality and effective protection. The Council of Europe as one of the oldest international organizations has joined the approach of codification and determination of the basic rules of civil and criminal responsibility for the commission of damages. Within this international organization during nineties of XX Century conventions were issued aiming to enhance the accountability system, rules to determine the responsibility, responsibility of entities and the sanctioning system under the condition that liabilities of the member states to incorporate these regulation into their national legislation. Having into account that our country is currently subject of essential reforms of policy, social, economic and legal system going towards the harmonization of internal regulations in compliance with the regulation or laws of the European Union, a special importance is deemed to be rapid adoption of environmental regulations (environmental law) and to be in compliance with the European law. Therefore, these conventions show a contribution towards a rapid and effective harmonization of our legal system with European legislation, especially when we have in mind the environmental risk in our country.

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management can sometimes hinder progress and cause confusion. This web site is designed to untangle and simplify these - to make environmental management using the above standards a much easier task.

<sup>13</sup> Carter Neli., The politics of the environment, Cambridge University Press 2001 pg. 321. Memorandums of Understanding have taken the form of customs from the late nineties of XX Century. There are more than 2000 MoUs concluded in Japan, Canada, and New Zealand. Based on EU data up to year 1997 there were more than 300 MoUs and the majority were concluded in Germany.

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## RATIONAL AND EFFECTIVE USE OF GEORGIAN REGION ARSENIC INDUSTRIAL WASTE FOR OBTAINING OF COMPOUNDS AND MATERIALS WITH SPECIFIC PROPERTIES\*

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### Abstract

*Arsenic is almost quantitatively educed from realgar(As<sub>4</sub>S<sub>4</sub>)-auripigment(As<sub>4</sub>S<sub>6</sub>) ores of Georgia, by an alkaline solution (NaOH, KOH). The process significantly accelerates if water solutions of the corresponding sulphides (Na<sub>2</sub>S, K<sub>2</sub>S) instead of alkali are used. The possibility of producing arsenic (III) sulfide from the industrial residuals of pyrometallurgical processing of nonferrous and precious metals ores is considered. For this purpose, the samples of industrial residuals of processing the nonferrous and precious ores were treated with amyl, izoamyl and hexyls alcohols. It is shown that the filtrate obtained from the mentioned samples can be used as an initial material for production of arsenic (III) sulfide. An expansion of practical application area, both for the mineral and production waste are determined.*

*Based on arsenic and stibium compounds obtained by transformation of arsenic industrial waste [arsenic(III) and stibium oxide, arsenic(III) and stibium chlorides and alkoxides we synthesized and studied new cationic-anionic complexes and chelates. The interaction of tetrasubstituted arsonium iodides, obtained based on Arsenic industrial waste products transformation, with zinc iodide and potassium cyanide was studied: from the wastes of arsenic industries and via their transformations, from industrial waste of pyrometallurgy production of arsenic we s obtained: White arsenic with high cleanness for use in pharmacopoeia;*

*We obtained new economic compounds and materials based on them. We fulfilled the technical order of business, definition of possibilities of creation of joint enterprises with limited liability. We synthesized and studied carbofunctional polymers with various structures, purposed for creation the matix component of antibiocorrosion coatings have been. By using the data of IR and NMR spectral analyses the composition and the structure of synthesized compounds have been established.*

*Based on matrix component and bioactive complex compounds we created various materials multifunctional application for individual and environmental protection. Based on the preliminary researches it was shown that the elaborated composites may be recommended as: a) protective covers of multifunctional destination (film materials and impregnating compositions) stable to biocorrosion; b) materials with antimycotic properties for prophylaxis and treatment of mycosis and dermatomycosis: adhesive compositions in the form polymer systems for nail fungi diseases treatment; c) biologically active polymer materials for crops protection, and also for human protection during contacts with microorganisms.*

*\*This paper dedicate to memory of our eldest friend and teacher Prof. Roman Gigauri.*

**Key words:** realgar-auripigment ores, eduction, arsenic (III) sulfide, matrix, bioactivity

### 1. Introduction

Utilization and purposeful use of industrial waste and secondary raw materials present significant technical-economical backlog for any country.

Waste pollution of the following three principal types is characteristic to Georgia region:

- Waste of chemical industry (including the factories not functioning currently, lithopone, barite, etc.):
- Leavings of procession of natural raw materials such as trachites, calcites, lithopone, barite, arsenic, industrial wastes, coniferous, nut-shell, etc.
- Secondary raw materials in the shape of non-recyclable items or packing from various polymers e.g., polypropylene, polyethylene, polychlorvinyl, polyethyleneterephtalat, etc.), which is linked with rapid development of tourism and growth of import in Georgia;

Purposeful recycling of the wastes is performed in two main directions:

1. Regeneration of precious compounds from the industrial wastes/leavings (Gigauri *et.al.* 2007);
2. Use of the industrial waste for creation of various compounds and materials with specific properties [Tskhakaia 1978, 3-18, and Brostow *et.al.* 2010, 159, 24-26].

Realgar ( $As_4S_4$ )-uripigment ( $As_4S_6$ ) ores of Racha (Georgia) are unique in the world [Luke 2000]. The content of a dominant in these ores is particularly high and reaches an average of 12% [Wolfson, Oshman, and Enikolopov 1990]. Besides, it is very important that these ores do not contain the impurity elements, and the best chance is given to produce not only highly pure metal arsenic and  $As_2O_3$ , but also other conversable products (Figure 2). For extracting arsenic and some of its compounds from the realgar-auripigment ores of Racha, first of all, the concentrate is burned in a special furnace that does not exclude pollution of environment both by sulphur dioxide and by arsenic compounds - 2-3% of aerosol comes on white arsenic (Wolfson, C.A., Oshman, V.G., Enikolopov, N.C. 1990).

Arsenic is also a natural associate element almost of all nonferrous and precious metals. After pyrometallurgical processing of the ores of these elements, which is one of the inevitable conditions for their recovery in an individual state, it comes out of the technological scheme in the form of white arsenic and is present in industrial residuals. The content of arsenic in them often varies within 8-60%. At the same time, they contain commercially important quantities of precious metal. To avoid environment pollution, the residuals are buried in a special burial ground (sepulchre) that is associated with great material and financial expenses.

Arsenic is almost quantitatively reduced from realgar ( $As_4S_4$ ) – auripigment ( $As_4S_6$ ) ores of Georgia, by an alkaline solution (NaOH, KOH). The process significantly accelerates if water solutions of the corresponding sulfides ( $Na_2S$ ,  $K_2S$ ) instead of alkali are used. The possibility of producing arsenic (III) sulfide from the industrial residuals of pyrometallurgical processing of nonferrous and precious metals ores is considered. For this purpose, the samples of industrial residuals of processing the nonferrous and precious ores were treated with amyl, isoamyl and hexyl alcohols. It is shown that the filtrate obtained from the mentioned samples can be used as an initial material for production of arsenic (III) sulfide. An expansion of practical application area, both for the mineral and production waste are determined.

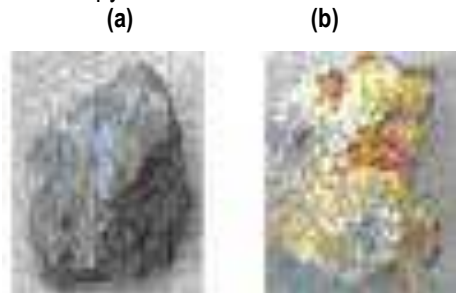
In mining-chemical factories odd the arsenic processing, chemically pure arsenic(III) sulfide designated for khalkogenic glasses, specified by semi conductive properties and employed in radio and television techniques were produced by a vacuum-thermal processing (Jokai, Hegoszki, and Fodor 1998), immediately from realgar-auripigment. Apart from the target product, realgar is also released as a secondary product, containing about 85-93 percents of the target product. Despite aforementioned the extraction technology of the arsenic and his satellite elements from the industrial waste of production of the realgar-uripigment and the application of the products, obtained from the former, are not studied perfectly by the present time.

There are important reserves in Georgia to extract arsenic from industrial wastes (arsenic-pyrite, realgar-uripigment processing and pyrometallurgical industry) in various forms in order to produce relatively cheap but important compounds [9-13] and materials with specific properties such



as pharmacevtral preparates, anthelmintes and antimicrobe conservers, etc.[2,14-18]. Real perspective appears for producing the arsenic-containing advanced – semi-conductors, anti-biocorrosional covers and biomedical nano composites [15- 18].

Last time there was attached the serious attention the possibility of the use some of arsenic compounds produced from the transformation industrial waste in homophate – in one of the interesting direction of the therapy.



**Figure 1.** The exhibits of Arsenic-pyrite (a) and Realgar-Uripigment (b) of Georgia

On the basis of analysis of literature data one concludes that apart from presence of many successful works on creation and investigation of functional compounds and composites based on arsenic industrial waste, there remain many problems, which demand solution. For example:

1. Creation of new cheap raw materials basis, which will be acceptable in technical, economical and ecologic view.

2. Use of industrial waste and secondary mineral resources for obtaining compounds, having either new or well-known structures, with specific, important properties and functional materials; to solve certain important technical problems with their help.

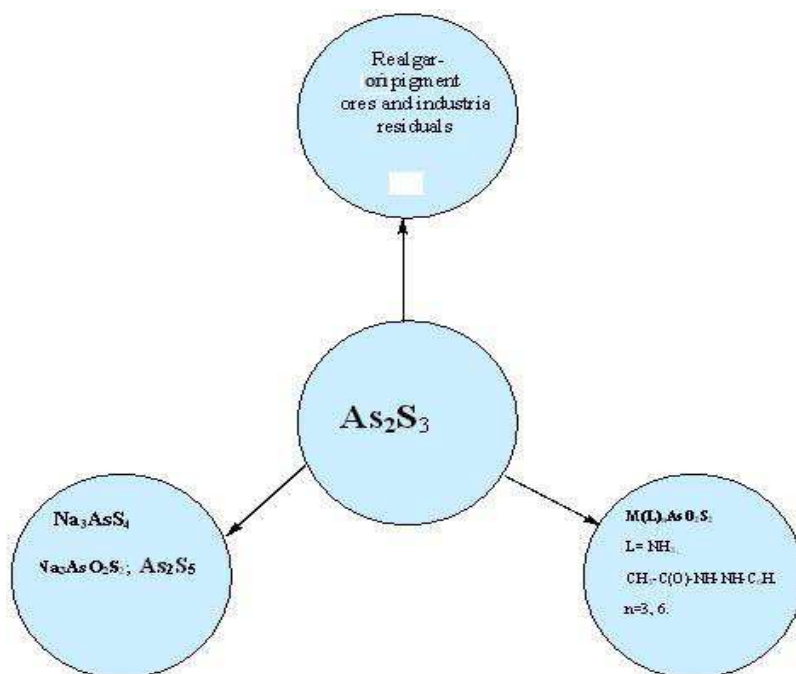
3. Research of the possibility to use of arsenic and stibium compounds based on the industrial waste of arsenic-pyrite, realgar-uripigment processing and pyrometallurgical industry in advanced non traditional technologies (nano composites, semy-conductors, optical-fibres communications, television techniques, non-silver photography etc.).

Realgar( $As_4S_4$ )-auripigment( $As_4S_6$ ) ores of Racha are unique in the world (Gigauri *et.al.* 2007); The content of a dominant in these ores is particularly high and reaches an average of 12% (Tskhakaia 1978, 3-18, and Brostow *et.al.* 2010). Besides, it is very important that these ores do not contain the impurity elements, and the best chance is given to produce not only highly pure metal arsenic, but also other conversable products. For extracting arsenic and its compounds from the realgar-auripigment ores of Racha, first of all, the concentrate is burned in a special furnace that does not exclude pollution of environment both by sulfur dioxide and by arsenic compounds - 2-3% of aerosol comes on white arsenic [Luke 2000].

Arsenic is also a natural associate clement almost of all nonferrous and precious metals. After pyrometallurgical processing of the ores of these elements, which is one of the inevitable conditions for their recovery in an individual state, it comes out of the technological scheme in the form of white arsenic and is present in industrial residuals. The content of arsenic in them often varies within 8-60%. At the same time, they contain commercially important quantities of precious metal. To avoid environment pollution, the residuals are buried in a special burial ground (sepultchre) that is associated with great material and financial expenses. There is possibility of producing arsenic (III) sulfide from the residuals of pyromctaliurgical processing of the ores of precious and nonferrous metals. Hence, at least two problems would simultaneously be solved: it would not be necessary to bury the arsenic-containing residuals and all expenses would be avoided, see Figure 1.

In Georgian region - Racha mining-chemical factory chemically pure arsenic (III) sulfide designated for khalkogenic glasses, specified by semi conductive properties and employed in Radio and Television (see ref [5]) technologies, were produced by a vacuum - thermal processing (Wolfson, Oshman, and Enikolopov 1990), immediately from realgar-auripigment. Apart from the target product, realgar is also released as a secondary product, containing about 85-93 percents of the target product. (The rest is  $As_4S_6$  and elemental sulfur). Despite all these, neither deposit realgar nor their application areas, as a production residue are not definite for the present time.

The aim of our research is to determine the possibility of arsenic removal from the realgar-auripigment ores and from the phytometalurgical residuals, by omitting the stages of the concentrate preliminary burn. The desired product arsenic (III) sulfide could be used in TV equipment, electrical and xerographic industries (Jokai, Hegoszki, and Fodor 1998), etc.



**Figure 2.** Realgar-uripigment (b) source of Georgia

As it is known zinc represents the most important element in many respects for all lives organisms. It is unchangeable for synthesis of ferment carbohydrate existing in erythrocytes, which is important for respiration processes.  $Zn^{2+}$  ions produce complex compounds near the ligands containing nitrogen and oxygen donor atoms that are interested in many respects because they are included in composition of active center of vital important ferment.

Zinc is included in all organs and materials of animal. It takes participation in production of active form of insulin and uses for assignment of hormonal activation of synthesized insulin. On the basis of this fact our purpose is to synthesis biologically active complexes which contain such biologically active elements as are arsenic, zinc, nitrogen and many other organic radicals. Follow from above mentioned we hope that coexisting of this elements increase physiological activity of synthesized complexes.

Application of arsonium salts for synthesis of coordination compounds keeps priority in chemistry of arsenic-organic compounds (Gigauri, Chachava, Gverdtsiteli, Laperashvili, 2007). They easily form cationic-anionic complexes (Tskhakaia 1978, 3-18, and Brostow *et. al.* 2010), soluble

salts of tetraalkyl(aryl)arsonium are successfully used for precipitation of ions (their common salts are highly soluble in water) [Wolfson, Oshman, and Enikolopov 1990]. It is known that d<sup>10</sup>-elements easily form pseudohalogenic acid-complexes with different composition and structure. On the basis of these facts, try to ascertain the coordination sequence of ligands and biologic activity of such compounds (Gigauri *et.al.* 2007).

Last decade the period of an intensive technical progress followed by creation of a new materials and appearance of aggressive microorganisms population. A lot of synthetic polymers and materials based on them are susceptible to attack of various microorganisms in the environment leading to product failure<sup>2</sup>. The actions of microorganisms on polymers are influenced by two different processes: a) the deterioration and degradation of polymers which serve as a native substance for growth of the microorganisms (direct action); b) the influence of metabolic products of the microorganisms. Losses of destruction of natural and synthetic materials with micromycets reach enormous amounts and constitute milliards of dollars annually in worldwide scale (indirect action).

One of the ways for protection of synthetic materials from the action of microorganisms is the creation of novel polymer covers with high bioactivity by modification of various polyfunctional film-obtaining adhesive polymer matrixes with biologically active compounds [Jokai, Hegoszki, and Fodor 1998].

Use of natural and synthetic biologically active compounds as modificating additives, unable to firm fixation in polymer matrix. Such polymers are characterized not only by contact [fungistatic] action, as the first ones, but can dosilly extract biologically active compounds to environmet. The latter is an important factor of guaranteed human protection during it long stay in a closed space.

In many regions of the world is widely circulated some diseases of agricultural plants, caused by various phytopathogenic microorganisms. For example, roots cancer, caused by *A. tunefacicus*. Tumors, halles and nodes are formed as a result of intensive division of affected cells of meristem plant tissues. Roots' and fruit-trees cancers are provoked by - *A. tunefacicus*; a cancer of root crops, beets is provoked by *X. campestris pv. Beticols*, etc. These diseases distractively damage plants and significantly decrease harvesting efficiency. They also deteriorate quality of grape, water-melons, melons and gourds and other agricultural plants [20].

Therefore synthesis of new compounds as plants protectors with high biological activities and effective for phytopathogenic microorganisms, as well as conservers and compounds for anti-biocorrosive covers of various natural, synthetic and artificial materials, cultural heritage is extremely significant and requires further development.

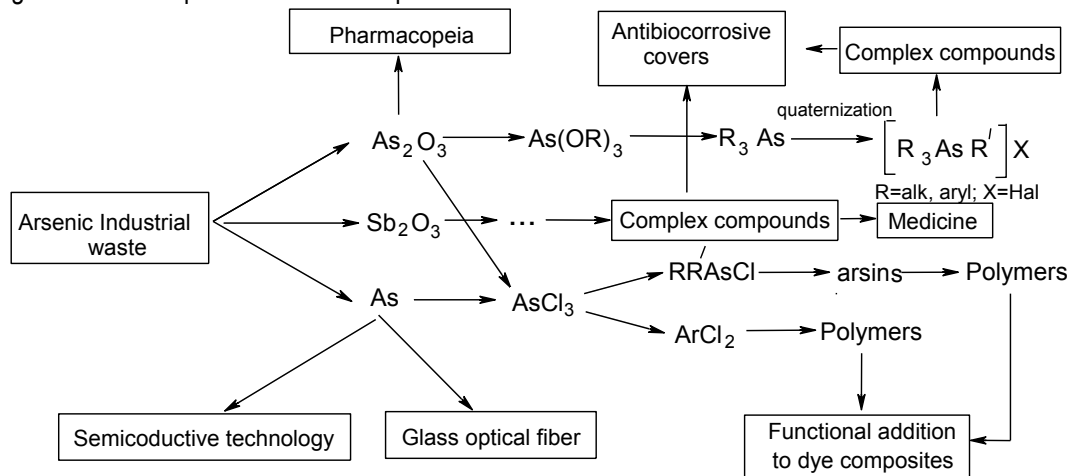


Figure 3. Scheme of the obtaining and using from arsenic industrial waste some of important arsenic and stibium containing compounds

## 2. Experimental

### Method of Analysis:

**Spectral analysis:** IR spectra were obtained from KBr pellets, using UR-20 (Karl Zeiss®) spectrophotometers and a Nicollet Nexus 470 machine with MCTB detector (Friebulin 1991). NMR spectra were obtained with an AM-360 (Brucker®) instrument at an operating frequency of 360 MHz using  $\text{CDCl}_3$  as a solvent and tetramethylsilane as an internal standard <sup>7</sup>.

**Elemental analysis** of the obtained compounds was carried out according to classic methods of micro elemental analysis (Kreshkov et al. 1962, and Sharlo 1965). The quantitative determination of functional groups was performed by using procedures described in ref. 23. The content of the active hydrogen in Si–H was determined according to Iwahara, Kusakabe, Chiba, and Yonezawa in 1993.

**Quantum-chemical calculations** were performed on PC with AMD processor with the built-in coprocessor by using Mopac2000 and CS Chem3D Ultra, v8. We gave the following key-words to guide each computation: EF GNORM=0.100 MMOK GEO-OK AM1 MULLIK LET DDMIN=0.0 GNORM=0.1 GEO-OK.

**Thermogravimetric and differential-thermal analysis** (TGA and DTA) was performed on a derivatograph (Paulic, Paulic & Erdey) at the speed of the heating  $10\text{Kmin}^{-1}$ .

**Chromatography analysis** of original reagents and the reaction products were performed by using the device LKhM-80 (Russia), type 2 (the column 3000 x 4 mm, the head – “Chromosorb W, the phase-5 mass % SE-30, and gas-carrier-helium).

**Wide-angle X-ray** diffractograms have been obtained by DRON-2 instrument (“Burevestnik”, Petersburg, Russia). Cu  $K\alpha$  was measured without a filter; the motor angular velocity was  $\omega \approx 2\text{deg.min}^{-1}$ .

**Test.** A cone-shaped, one-liter flask, fitted with an agitator with heater and a dropping funnel, is charged with a 100-g specimen containing 7.5% As to be added with 500 ml *Thiobacillus ferrooxidans* culture solution and 50 ml, under conditions of continuous agitation and aeration and at the 20-25° C temperature during 48 hours at least. Maximum in 60 hours, the oxidation-recovery of arsenic in the culture solution will occur. If in the course of the process the solution quantitatively reduces, an acidified water ( $\text{H}_2\text{SO}_4$  or  $\text{HCOOH}$ ) pH=1.5-2.5 will be added. The leached bacterial solution is filtered. The filtrate is placed in a measure bottle. An aliquot portion of the solution (5 or 10 ml) is taken for analysis; after it has been dried, the percentage of arsenic is determined in the dry residue by the Evans method, being based on the iodometric titration in the low-alkalinity medium. It is calculated by the formula:

$$\text{As}\% = \frac{V \cdot 0,1873}{g},$$

where  $V$  is the spent volume in ml,  $g$  is the weight unit.

The yield of arsenic in the dry residue totals 96.5%.

Thus, as a result of the conducted research, a new promising method of bacterial-chemical leaching of arsenic has been developed to enable practically the processing of thousands of tons of arsenic-containing waste and recovery from it pure arsenic compounds.

The solid mass cleaned from the dominant element (containing 0.5-0.6% arsenic) is a concentrate of noble metals, in particular of gold, whose bacterial-chemical oxidation is the follow-up stage of our research.

### 3. Results and discussions

#### 3.1. Arsenic education from realgar – Auripigment ores of Georgia

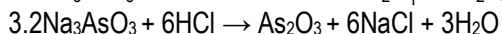
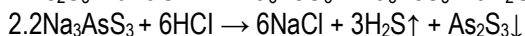
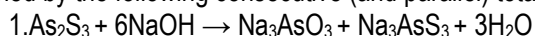
In order to solve the raised problem, we have focused our attention on the property of natural arsenic sulfide forms - to dissolve in alkalis and to form the compounds soluble in water that will give the possibility to remove them from the insoluble residue by filtration.

As an object of the investigation we chose the samples of Lukhuni (Georgia) mine. After pulverizing and sieving the sample, we performed chemical analyses on the content of arsenic and sulfur. Arsenic was determined using the method of Ewins, as for sulfur, it was determined by the gravimetric method (Sharlo 1965). On the whole, we investigated 6 (six) samples of the realgar-auripigment ore with the total content of arsenic: % weight 6.8 (I); 11.4(II); 14.2(III); 18.9 (IV); 23.0 (V) and 41.0 (VI). The atomic ratio of arsenic and sulfur in the investigated objects was mainly equal to 2:3, however, by sight the content of realgar in them should have been one third of auripigment. This fact points to the following: the impurity elements must also be present in the investigated objects mainly in sulfide forms. The results of chemical analyses of samples I, II and IV on the content of sulfur point to the same fact: the content of sulfur turned out to be larger by 2% that shown by the As:S = 2:3 ratio.

By a number of experiments, it was established that it is quite possible to educe the sulfide forms of arsenic from the realgar-auripigment concentrates by means of alkaline solutions provided that, for eduction, such an amount of solution is taken that the hydroxide-arsenic ratio will be 3:1. Moreover, more complete eduction of the desired product is achieved in the case when, for reaction the alkali is taken in an amount by 5-10% more than the theoretical one. As the reaction is heterogeneous, the degree of eduction, as it was expected, strongly depends on the division degree of the realgar-auripigment concentrate and on the suspension temperature (of course, if the above-mentioned arsenic-alkali ratio is fulfilled). Namely, concentrate IV with the 18.9% content of arsenic sifted in 1.00; 0.50; and 0.25 mm sieves was studied. It turned out that, if the realgar-auripigment suspension with 1.00 mm diameter needs 4 hours to reach the equilibrium in the alkaline solution, from the same amount of the concentrate sifted in the 0.25mm sieve, the maximum eduction is reached in 1 hour, of course, in case of intensive stirring of the suspension.

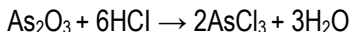
So, the maximum arsenic eduction is reached in case of the sample division to 0.25 mm. Under such conditions, the degree of the arsenic eduction, which we determined experimentally, varies within 97.0-99.7%. This degree of the arsenic eduction was determined by the analyses of the solid residue remained after the suspension filtration. In all other cases, as the investigation showed, it is necessary to increase the division degree of the residue and to educe it by alkali once more with the same ratio of reagents. In this case, the residue remained after the eduction does not contain the amount of arsenic which can be dangerous for the environment. Even it's keeping on tile open ground is possible from the ecological point of view.

As for the dependence of the degree of the arsenic eduction from the realgar-auripigment ore on the alkali concentration, it should be mentioned that, for its determination, 5; 12 and 20% sodium alkali was used. It turned out that, for the concentrates of the same composition and the division degree, the eduction degree practically does not depend on the alkali concentration if the total amount of the tatter corresponds to the above-mentioned ratio. The eduction degree does not depend on the kind of alkali either. Thus, it will be expedient to use sodium alkali instead of a potassium one as a cheaper and more available reagent. Treating the filtrate (pH>4) by acid (HCl, H<sub>2</sub>SO<sub>4</sub>), the mixture of arsenic (III) sulfide and white arsenic is settled, formation of which must be explained by the following consecutive (and parallel) totality of reactions:



The same result is achieved at filtrate neutralization by sulfuric acid.

From the presented equalities, it follows that the white arsenic - diarsenic trisulfide ratio in the mixture is 1:1. In fact, the molar portion of  $As_2S_3$  strongly exceeds the one of white arsenic that can be explained by good solubility of the latter in hydrochloric acid [Brauer 1985]:



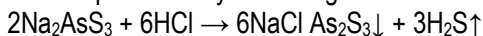
As, under the same conditions (Gigauri, Kamai, and Ugulava 1971), arsenic sulfide does not affect hydrochloric acid at all if a sufficiently large amount of the latter is taken for the reaction, entire removal of the white arsenic impurity from trisulfide becomes possible. As for treatment of the filtrate by sulfuric acid, though, in this case, the increase in the sulfide form molar portion in comparison with the oxide forms is observed, but not in such way as it is reached in the case of hydrochloric neutralization, it is evident that this fact also must be explained by comparatively weak solubility of white arsenic in the sulfuric acid medium.

Much better results of the arsenic eduction from the realgar-auripigment concentrates is achieved when the sodium sulfide solution is used. In this case, both the solid phase division degree and the molar ratio of reagents are of a decisive significance. If this condition is fulfilled, the eduction process proceeds at a room temperature during 1 hour. It seems that the goal is achieved by the following totality of consecutive reactions]:



Before starting the experiment, the equivalent amount of the sodium alkali water solution is saturated by hydrosulfur. Then, the well pulverized and sieved realgar-auripigment concentrate is added to it. The reaction mass is filtered after one hour of intensive stirring, the residue is washed by 1% alkali, then by water. After this, the residue is dried on air until getting the constant mass and analyzed. The degree of adduction is almost quantitative, if for adduction, the concentrate sifted in, the 0.25 mm sieve is taken.

As the result of the filtrate treatment by acid to a strong acid medium ( $pH \geq 3$ ), orpigment is settled almost quantitatively according to the following equality;



The isolated hydrosulfur can be used again to get the resulting sodium sulfide, etc. This method of arsenic (III) sulfide production from the realgar-auripigment ores takes the continuous and cyclic character. The content of the main product ( $As_4S_6$ ) in the dry residue is 97-99% that should be considered as a good result [12 -26]. The results of the spectral Quantitative analyses of arsenictrisulfide extracted from the realgar-auripigment ore, which contains 23% of arsenic (V), on the content of impurities is presented in the Table.

**Table 1.** The results of the  $As_2S_3$  spectral analyses

Sample	Content of impurities , %						
	Al	Cu	Fe	Mn	Mg	Sb	Si
$As_2S_3$	$2 \cdot 10^{-5}$	$1 \cdot 10^{-5}$	$2 \cdot 10^{-5}$	$1 \cdot 10^{-5}$	$1 \cdot 10^{-5}$	$2 \cdot 10^{-5}$	$5 \cdot 10^{-5}$

As it is evident from the presented Table 1., the content of impurity elements in the sample is not high and corresponds to the composition of arsenic (III) sulfide produced by direct synthesis.



So, the experimental results make it simply evident that it is possible to extract arsenic(III) sulfide almost quantitatively from the realgar-auripigment ores as the result of reduction of alkaline metal sulfide if the filtrate is treated by hydrochloric or sulfuric acid to the strong acid medium ( $\text{pH} \geq 3$ ).

### 3.2. Arsenic education from industrial residuals

As the object of research, we chose the arsenic-containing residuals of nonferrous metals brought from Novosibirsk and the residuals of precious metals had brought from Ural to Racha Mining Chemical Plant for processing.

It was shown (Kuzmin, 1954) that the interaction between high series monoatomic alcohols and white arsenic is a clearly expressed selective reaction - the alcohols seems to "look for" arsenic(III) oxide and forms arsenic acid ether with it, but it leaves all other admixtures without any attention.

Basing on this fact, we treated industrial residuals with amyl, izoamyl and hexyl alcohols. It was found out that, from all the mentioned natural admixtures, maximum arsenic is extracted by the method of azeotropic drying. In the residual (raffinate), the As content varies within 0.64 -1.07%, if the alcohol taken for reaction is by 3% more than the theoretical value,



The results of the spectral quantitative analysis of the samples and the corresponding raffinates on the content of admixtures are presented in Table 1. It is clearly seen that, after arsenic extraction the content of precious metals in the raffinate sharply increases, that in its turn, can become the base for gold production.

Loading of the obtained substances and quantities of the extract filtrate along with the results of the analysis on the arsenic content are presented in Table 2. It is clear, that the content of arsenic in the filtrate does not depend on the initial residual and the alcohol quantity - the result is always the same if the following condition is satisfied: in the initial mixture arsenic must be in the form of oxide.

It was established that the filtrate can successfully be used an initial material for producing arsenic (III) sulfide. The aim is achieved according to the reaction:



To completely settle arsenic (III) sulfide, after completing the process, we neutralized the reaction mass by hydrochloric acid up to the strong acid medium ( $\text{pH} \geq 3$ ). So, the output of the desired product varies within 81-85% that is rather reasonable for industrial conditions. From reaction (2), it is also evident that almost the same amount of alcohol is recovered that makes it possible to use it again for extracting arsenic from the industrial residuals, etc. Thus, the process will have the continuous and, at the same time, circular character.

The optimum conditions of the interaction of white arsenic with high series monoatomic spirit and, therefore, of arsenic extraction from the mixture are described in work (Gigauri, Kamai, and Ugulava 1971).

**RECOVERY OF AHSENIC (III) SULPHIDE** Into the 0.5 l Erlenmeier flask with a ground lid, in which there were 80.3 g of sodium sulphide  $\text{Na}_2\text{S} \cdot \text{H}_2\text{O}$ , we added 100 g of the extract obtained by treating Raffinate N with amyl alcohol. The substance inside the flask was treated with distilled water (100 ml) after intensive magnetic stirring during an hour. Two layers were formed: the lower layer - a water solution, from which a small quantity of yellow sediment as isolated, and the upper layer- amyl alcohol.

For completing the process the reaction mixture was heated up to 80-90°C during an hour. After cooling, we separated the layer of alcohol and the layer of water which we neutralized with 21% hydrochloric acid. Fine-crystalline yellow sediment was formed. It was separated from the initial solution to pH=3, was well washed with water, and was dried in air until getting the constant mass.

If we base on the results of the arsenic analysis, the basic product content in the researched object makes up 98.7%. That correlates well with the chemical content of arsenic(III) sulfide obtained by direct synthesis.

Recovered amyl alcohol was 74.7% or 92.2% of the theoretical value. Other experiments were carried out similarly. Their results are presented in Table 3.

The total content of arsenic was determined by the Ewins method (Freidlina 1945), but the sulfur content - by the weight method (Brauer 1985).

The optimum conditions of the interaction of white arsenic with high series monoatomic spirit and, therefore, of arsenic extraction from the mixture are described in work (Gigauri, Kamai, and Ugulava 1971).

**RECOVERY OF ARSENIC (III) SULPHIDE** Into the 0.5 l Erlenmeyer flask with a ground lid, in which there were 80.3 g of sodium sulphide  $\text{Na}_2\text{S} \cdot \text{H}_2\text{O}$ , we added 100 g of the extract obtained by treating Raffinate N with amyl alcohol. The substance inside the flask was treated with distilled water (100 ml) after intensive magnetic stirring during an hour. Two layers were formed: the lower layer - a water solution, from which a small quantity of yellow sediment was isolated, and the upper layer - amyl alcohol.

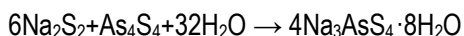
For completing the process the reaction mixture was heated up to 80-90°C during an hour. After cooling, we separated the layer of alcohol and the layer of water which we neutralized with 21% hydrochloric acid. Fine-crystalline yellow sediment was formed. It was separated from the initial solution to pH 3, was well washed with water, and was dried in air until getting the constant mass.

### 3.3. Arsenic utilizing production waste

In the capacity of original material, we used realgar auripigment ore-containing deposits of Racha and production waste containing the same matter.

Selection and sorting of the mineral realgar have been carried out manually, mechanically: having ensured visually that the object included impurities, we ceased taking the sample. As for the realgar, as one of the basic components of the arsenic (III) sulfide production waste, in the Racha mining-chemical factory, 5 parties of it had been brought from the mentioned factory..

It has been determined that chemical pure realgar, selected in the Lukhuni deposit, is easily oxidized by sodium disulfide, producing the corresponding trivalent arsenate. The reaction, as it has turned out is expressed by equation:



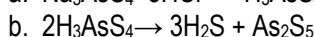
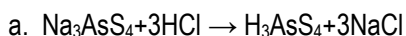
The tests have been conducted in water solutions.

For oxidation we used two parties of the production waste with 85.91 and 92.94% realgar content (the rest-auripigment). As it has turned out, if the sodium disulfide and the production waste are taken for the reaction, in quantities enough to ensure that sodium and arsenic correlate as 1:3, the production waste mentioned above is as better for sodium trivalent arsenate production, as the chemical pure realgar. The target product release, as it seems, should be explained by combination of following consequent reactions:

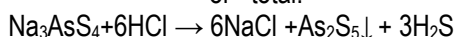


For the reaction a-modification of sodium disulfide containing about 4% of ethyl alcohol is used. That is exactly why: this reagent is practically taken in 4-5% more than it is provided for in the theoretical part. The sulfur released in the course of reaction (2) covers the bottom of the reactor, the mother solution is removed by way of filtering, as regards the filtrate, it is carefully evaporated till appearance of a crystal film on walls and the surface. This is the way the chemically pure sodium tetrathio arsenate is produced.

The same production waste can become a base for arsenic(V) sulfide production. With this purpose it is enough, remove from the sodium disulfide and the waste interaction product the excessive sulfur by way of filtering, and the filtrate be processed with an acid (HCl, H<sub>2</sub>SO<sub>4</sub>) until a strong acid reaction (pH=2-3). As a result, a diarsenic pentasulfide precipitation is released. Formation of this last should be explained, as it turns out, through a combination of following consecutive reactions:



or total:



Release of gas sulfur hydrosulfide is detected by odor or by way of running lead (II) nitrate water solution; -release of a black, insoluble residue is the sign of hydro sulfide presence. For better understanding of the above mentioned particular examples are brought.

Sodium tetrathio arsenate Na<sub>3</sub>AsS<sub>4</sub> synthesis:

Into 100 ml, Erlenmeyer flask with a ground stopper, 4.28 g of well powdered realgar is placed and 6.94 g, sodium sulfide light yellow color powder. The content of the flask is promptly added with 60ml of Bidistillate and intensely stirred. The oxidation is a clear cut exothermic reaction, as far as the participating mass temperature exceeds 50°C. In order to terminate the process, the participating mass is being heated up in air tight environment for an hour at 60-70°C. After cooling, the mass is being filtered in order to get rid of insignificant, but visually still noticeable mechanic impurities. While the yellowish filtrate is carefully evaporated in a quartz cup, until appearance of a colourless, crystal film on the solution surface. The solid mass is separated by use of a water pump and washed with alcohol. After being dried on open air till the constant mass 14.4 g. almost colourless sodium tetrathio arsenate is received, this amounts to 87.0 % of the theoretical reckoning

**Table 2.** The results of spectral quantitative analysis of industrial residuals and raffinates

No	Sample	Treatment with spirit ROH. where R	Element content												
			Au g/t	Ag g/t	Fe	Cu	Mn	Zn	Ni	Pb	Cd	Na	K	Co	As
1	Raffinate N	-	2.0	4.0	1.5	0.009	0.07	0.02	0.02	0.03	0.002	0.035	0.077	0.01	56.13
2	Raffinate I	izo-C <sub>5</sub> H <sub>11</sub>	18.3	26.0	13.7	0.006	0.05	0.048	0.01	0.12	0.002	0.15	0.44	0.06	1.07
3	Raffinate II	N-C <sub>5</sub> H <sub>11</sub>	16.0	21.0	9.1	0.061	0.04	0.11	0.008	0.13	0.0011	0.153	0.40	0.06	0.75
4	Raffinate U	-	1.0	8.5	3.6	0.029	0.074	0.037	0.004	0.22	0.0017	0.035	0.035	0.01	4196
5	Raffinate III	izo-C <sub>5</sub> H <sub>11</sub>	2.2	36.0	27.1	0.41	0.58	0.25	0.06	1.5	0.007	0.12	0.12	0.01	0.64
6	Raffinate IV	N-C <sub>5</sub> H <sub>11</sub>	2.0	33.0	25.2	0.163	0.54	0.14	0.019	1.4	0.0096	0.12	0.12	-	0.72

**Table 3.** Data on the initial substances and the obtained filtrate

Initial substances							Obtained filtrate		
Residual				ROH			Conventional I No.	g	As. %
No	Name	g	As.%	R	g	mole			
1	Raffinate N	100	56.13	C <sub>5</sub> H <sub>11</sub>	256	2.91	I	290	18.96
2	"	150	"	izo-C <sub>5</sub> H <sub>11</sub>	385	4.37	II	336	18.50
3	"	100	"	C <sub>6</sub> H <sub>13</sub>	296	2.90	III	330	16.67
4	Raffinate U	200	41.96	C <sub>5</sub> H <sub>11</sub>	383	4.35	IV	444	18.45
5	"	100	"	izo-C <sub>5</sub> H <sub>11</sub>	192	2.18	V	220	18.64
6	"	100	"	C <sub>6</sub> H <sub>13</sub>	222	2.18	VI	250	16.40

We obtained 25.3 g of arsenic(III) sulphide, that is 81.3% of the theoretical value. Obtained, %: As 60.21; S 38.17. From  $As_4O_6$ , calculated, %: As 60.97; S 39.02

**Table 4.** Quantities data on the initial and obtained substances

Initial substances				Obtained substances					
Filtrate		$Na_2S \cdot H_2O$		ROH			$As_2S_3$		
No	g	g	mole	g	mole	%	g	Mole	%
I	100	80.3	0.84	74.7	0.85	92.2	25.36	0.10	81.3
II	200	160.0	1.67	148.0	1.68	90.8	51.39	1.21	84.7
III	150	113.7	1.18	110.2	1.25	90.0	23.52	0.09	85.0
IV	100	80.0	0.83	75.0	0.73	89.7	22.11	0.09	82.2

#### Sodium tetratio arsenate $Na_3AsS_4$ synthesis:

Into 100 ml, Erlenmeyer flask with a ground stopper, 4.28 g of well powdered realgar is placed and 6.94 g, sodium sulfide light yellow color powder. The content of the flask is promptly added with 60ml of Bidistillate and intensely stirred. The oxidation is a clear cut exothermic reaction, as far as the participating mass temperature exceeds 50°C. In order to terminate the process, the participating mass is being heated up in air tight environment for an hour at 60-70°C. After cooling, the mass is being filtered in order to get rid of insignificant, but visually still noticeable mechanic impurities. While the yellowish filtrate is carefully evaporated in a quartz cup, until appearance of a colorless, crystal film on the solution surface. The solid mass is separated by use of a water pump and washed with alcohol. After being dried on open air till the constant mass 14.4 g. almost colourless sodium tetratio arsenate is received, this amounts to 87.0 % of the theoretical reckoning.

Practically we have %: As 17.98;  $H_2O$  34.11.  $Na_3AsS_4 \cdot 8H_2O$

Theoretically reckoned % is: As 18.09;  $H_2O$  34.60.

In the same way other tests have also been conducted, in order to produce sodium tetratio arsenate. Loading of the original material and the target product output is brought in the Table 3.1. Whence we conclude, that the output is high and almost in no dependence upon what has been used as the original material-chemically pure realgar or the production waste. In all cases, the output ranges from 86 to 93%, which by almost 20% exceeds.

Arsenic (V) sulfide production: Under the conditions described above, filtrate received through interaction of 8.8 g of the production waste (containing 92.9% realgar and 7.1% Origment) and 14.0 g. disulfide is processed with 20% hydrochloride acid until having PH=2. Immediately is released a loose, yellow coloured substance, which is being rested in the mother liquor during a nigh. The precipitate is filtered, washed carefully with water and dried in diphosphorus pentaoxide vacuum exicator, until the constant mass 12.6 g of diarsenic pentasulfide is produced, which is 95.9% of the theoretical reckoning,

Produced % is: As 47.93.  $As_2S_5$

Theoretically reckoned % is: As 48.31.

With the same order other tests have also been conducted in order to obtain diarsenic pentasulfide, which we do not describe deliberately, since the results are quite similar. It should be noted that the obtained arsenic sulfide Ir. spectrum turned out identical with diarsenic(V) pentasulfde IR spectrum [5], when this diarseic pentasulfide has been obtained in a strong acid environment.

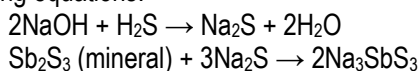
**Table 5.** Loading of original substances and outcome of target product

#	Loading of original substances								
	Sample	G	Realgar		G	Mol	Got Na <sub>3</sub> AsS <sub>4</sub> ·8H <sub>2</sub> O		
			Conten				G	Mol	%
			As <sub>4</sub> S <sub>4</sub>	As <sub>4</sub> S <sub>6</sub>					
1	Min. origin	4.3	100	0	6.94	0.063	14.48	0.035	87.0
2	"	8.6	100	0	12.88	0.126	30.83	0.074	92.6
3	Prod. waste	5.0	85.91	14.09	7.86	0.071	17.00	0.041	85.9
4	"	10.0	85.91	14.09	15.72	0.143	35.00	0.084	88.4
5	"	8.8	92.94	7.06	14.00	0.127	32.46	0.078	92.0
6	"	4.4	92.94	7.06	7.00	0.063	16.10	0.039	91.3

### 3.4. Separation of the Stibiumimpotant compounds from Georgian region industrial waste

Extraction of stibium from its industrial waste is of large technical and economical importance. A further treatment of stibium containing concentrated solutions obtained by the process of extraction allows isolating stibium compounds in a chemically pure state. In this case our goal is to obtain the complex compounds of some d(III) metal (Sc, Fe, Y, La) tetratiostibates(V) with 2,2'-dipyridile (dipy).

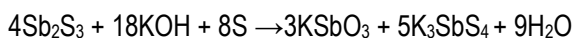
An extraction process of stibium from its minerals is produced using several hydro-chemical methods. The granulated ore is passed though the 0.40 mm sieve. Then, it is interacted with concentrated sodium hydroxide. The suspension is saturated by H<sub>2</sub>S (3-4 times more than theoretical) to avoid the forming of mixed Oxotiestibiat. The process takes place according the following equations:



After treating the filtrate by concentrated inorganic acids (HCl, H<sub>2</sub>SO<sub>4</sub>) chemically pure stibium(III) sulfide is regenerated.

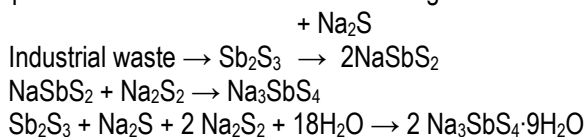
In the next stage stium(III) sulfide is converted into Tetratiostibiat. For this purpose several hydro-chemical methods are used:

**Method I Hydro-chemical treatment in presence of potassium hydroxide.** Stibium(III) sulfide is treated by the concentrated potassium hydroxide water solution . Than the suspension is heated and elemental Sulfur is added as an oxidative agent. The process is based on the following equation:



As a result of this method potassium stibiate is precipitated and, of course, the yield of potassium tetratiostibiat is low.

**Method II Hydro-chemical oxidation using sodium disulfide.** Disulfide of sodium promotes the maximal extraction of Antimony sulfide from its minerals and it can be directly used for this purpose. This method is based on following reactions:

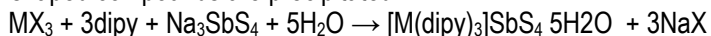


This method is characterized with the high yield of goal product (>70%).

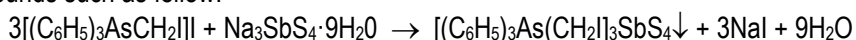


**Synthesis of the complex compounds of some d(III) metal (Sc, Fe, Y, La) tetratioantimonates(V) with 2,2'-dipyridile.**

The complex compounds of some d(III) -metals (Sc, Fe, Y, La) with 2,2'-dipyridile are obtained by the reaction of corresponding water soluble metal salts and 2,2'-dipyridile. Than without isolating dipyridilates the system is treated by sodium tetratioantimonate (V) and coloured, small crystal-shaped compounds are precipitated.



Based on obtained synthesized salt we also synthesized the new bioactive complex compounds such as follow:



The composition and structure of synthesized compounds we established based on data of elementary analysis, IR spectra and mass-spectra (As-Sb-complex).

**3.5. Synthesis and investigation of potassium – tetrasubstituted arsonium tetracyanozicates (II)**

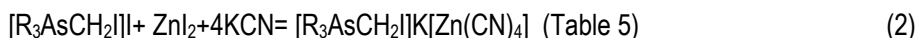
Our purpose was to study hydro-chemical interaction of tetra substituted arsonium (obtained from industrial waste products transformation) and zinc iodides in solution, in potassium cyanide. Experiments were carried out at room temperature (Nasibulina 1978, and Robaqidze 1997). In the aqueous solution of zinc iodide and potassium cyanide, under permanent agitation, alcoholic solution of tetrasubstituted arsonium iodide was added, initial compounds were taken in molar ratio  $[R_3AsCH_2I]: ZnI_2: KCN = 2:1:4$ . KCN was used 10-20% surplus in compassion with theoretical amount. Instantly- after mixing the solutions of initial compounds-white crystalline substance was formed.

As cadmium iodide easily forms acy-complexes with tetra substituted arsonium iodide [9], we expected to obtain cationic-anionic coordination compounds according the scheme:



But on the basis of elementary analysis it was established that 1atom-mole arsenic corresponds to 1-atom-mole of iodide (but not to 3, as according to the scheme 1).

Like that in the presence of excess amount of potassium cyanide, formation of the products of interaction of iodmethylentrialkyl(aryl)arsonium iodide and zinc iodide can be explained by the scheme:



The composition of synthesized compounds was established by physical and chemical and elementary analysis methods. Namely, the molar electro-conductivity was studied in the solution of dimethyl formamide. According to the Table 6,  $\mu$  changes in the interval  $77-92\text{ om}^{-1}\text{cm}^2\text{mol}^{-1}$ . This data is higher for bi-ionic complexes, but less than for tri-ionic complexes. Analogical occurrence was registered in [9] and authors explain this fact by partial coordination of anions by complex forms. Thus  $[Zn(CN)_4]^{2-}$  ions are, partially, associated with arsonium ions and its courses the decrease of electroconduction of the solution. Thus, in the solution such process can be realized:



In IR - specters (Nakamoto 1991) of the synthesized compounds (Figure 1), the absorption bands are detected at 430 and 515 $\text{cm}^{-1}$ , and this due by  $\nu$  (MC) and  $\delta$  (MCN) vibrations. The absorption band of As - $\text{C}_{\text{alk}}$  is detected at 630 $\text{cm}^{-1}$  and it indicates, that As is in  $\text{sp}^3$  hybridization state. The adsorption band of coordinated CN group  $\nu$  (CN) is detected at 2610 $\text{cm}^{-1}$ .

**Table 6.** Some characteristics of synthesized complex compounds  $[\text{R}_2\text{As}(\text{R}')\text{CH}_2\text{I}]\text{K}[\text{Zn}(\text{CN})_4]$

#	R	R'	Melting point, t, °C	Molar electroconductivity $\text{om}^1.\text{cm}^2.\text{mol}^{-1}$	Was found %				Brutto-formula	Calculated %			
					As	Zn	N	I		As	Zn	N	I
1	C <sub>4</sub> H <sub>9</sub>	C <sub>6</sub> H <sub>5</sub>	150-151	83,6	11,86	10,24	8,85	20,41	C <sub>16</sub> H <sub>15</sub> AsKZnNI	12,19	10,56	9,10	20,65
2	C <sub>4</sub> H <sub>9</sub>	C <sub>4</sub> H <sub>9</sub>	170-171	92,0	12,56	11,02	9,24	20,98	C <sub>17</sub> H <sub>15</sub> AsKZnNI	12,60	10,92	9,41	21,34
3	iso-C <sub>4</sub> H <sub>9</sub>	izo-C <sub>4</sub> H <sub>9</sub>	234-235	95,1	12,43	10,78	9,71	21,56	C <sub>17</sub> H <sub>15</sub> AsKZnNI	12,60	10,92	9,41	21,34
4	C <sub>5</sub> H <sub>11</sub>	C <sub>6</sub> H <sub>5</sub>	122-123	80,3	11,81	9,84	8,65	19,65	C <sub>18</sub> H <sub>15</sub> AsKZnNI	11,66	10,10	8,70	19,75
5	C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub>	236-237	77,6	11,33	9,90	8,50	19,21	C <sub>22</sub> H <sub>17</sub> AsKZnNI	11,45	9,92	8,54	19,38

**Table 7.** The quantities of initial compounds for obtaining tetrasubstituted arsonium tetracyanozincates(II)

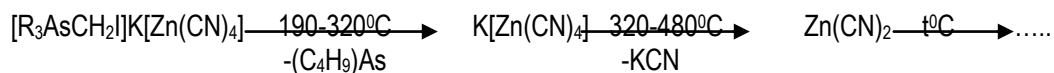
#	For the reaction iodomethylenetrialkyl(aryl)arsonium was taken								Yield		
	[R <sub>2</sub> As(R')CH <sub>2</sub> ]I				ZnI <sub>2</sub>		KCN		[R <sub>2</sub> As(R')CH <sub>2</sub> ]K[Zn(CN) <sub>4</sub> ]		
	R	R'	g	mol	g	mol	g	mol	g	mol	%
1	C <sub>4</sub> H <sub>9</sub>	C <sub>6</sub> H <sub>5</sub>	2,5	0,0046	0,74	0,0023	0,73	0,0112	1,23	0,0020	86,5
2	izo-C <sub>4</sub> H <sub>9</sub>	izo-C <sub>4</sub> H <sub>9</sub>	2,5	0,0048	0,77	0,0024	0,75	0,0116	1,21	0,0020	84,3
3	C <sub>5</sub> H <sub>11</sub>	C <sub>6</sub> H <sub>5</sub>	3,0	0,0053	0,85	0,00265	0,83	0,0128	1,36	0,0021	79,6
4	C <sub>4</sub> H <sub>9</sub>	C <sub>4</sub> H <sub>9</sub>	2,5	0,0048	0,77	0,0024	0,75	0,0116	1,17	0,0019	80,9
5	C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub>	3,5	0,0060	0,97	0,0030	0,95	0,014	1,66	0,0025	83,2

Below we give the roentgen-phase (X-ray) analysis data for synthesized complex compounds (Table 8).

**Table 8.** Results of the Roentgenographic (X-ray) analysis of synthesized complex compounds

Complex compound [(C <sub>5</sub> H <sub>11</sub> ) <sub>2</sub> As(C <sub>6</sub> H <sub>5</sub> )CH <sub>2</sub> ]K[Zn(CN) <sub>4</sub> ]					
№	Intensity, I/I <sub>0</sub>	d <sub>a</sub> /n	№	Intensity, I/I <sub>0</sub>	d <sub>a</sub> /n
1	100	12.03	9	10	3.24
2	20	10.4	10	30	3.19
3	30	5.9	11	15	3.07
4	35	4.56	12	20	2.60
5	25	4.33	13	25	2.56
6	30	4.05	14	5	2.36
7	20	3.63	15	10	2.31
8	15	3.49	16	5	2.23

Thermolysis of the synthesized compounds was studied (Fig. 4). The sample, in 190-320°C interval loses 76.17% of its mass, that indicates at the loss of whole "organics" (theoretically 69.44%); loss of the mass in 320-480°C interval is equal to 10.78%-one mole KCN is separated (theoretically-10.92%). The scheme of thermolysis can be presented as:



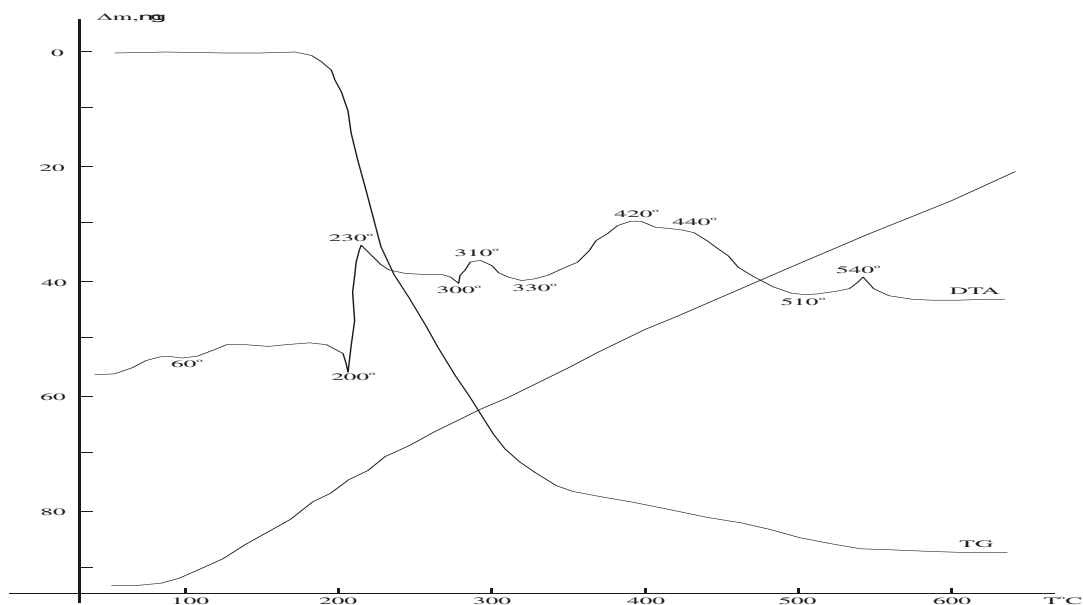


Figure 4. Thermogram of  $[(C_4H_9)_3AsCH_2]K[Zn(CN)_4]$

### 3.6. Bacterial – chemical leaching of arsenic from arsenic containing waste

Arsenic is a distinguished natural resource of Georgia being reflected in its large reserves and unique chemical composition contained in the *Racha* realgar ( $As_4S_4$ ) orpiment ( $As_4S_6$ ) and *Tsani* arsenopyrite ( $EeAsS$ ) ores. It is the very ores from which white arsenic ( $As_2O_3$ ) metallic arsenic and its high-purity compounds used to be recovered. The content of arsenic in the ores varies from 1-30% to 7.5% on the average (Nakamoto 2004).

White arsenic is the ore-recoverable material, the yield of which makes 87-94%. Due to technical problems, up to 3-7% remained unrecoverable in the form of the white arsenic “tails”. This problem has not been solved up to now and its results are the polluted environment – the whole production area and its adjoining territory, the River *Tskhenis Tskali* (Gigauri 2004). In our opinion, these problems can be handled through actions in the following two directions:

(a) The “tails” formed as a result of the processing of ores (which also contain nonferrous and noble metals) should be placed into special bunkers to prevent their contact both with oxygen and water;

(b) After the dominant element (arsenic) has been removed, the remaining material could be utilized as a concentrate of noble metals.

The second direction (b), envisaging the bacterial-chemical leaching of arsenic from the production waste, seems to be much more promising. All the arsenic-containing waste, which will be required for future studies, has been initially analyzed; the percentage of arsenic in them has been determined by the Evans method. As a result, the samples have been found to contain a part of arsenic in the form of arsenite. The presence of these elements as oxides or carbonates is not excluded as well (Khidasheli 1996). The Table no 9 presents a spectral-quantitative analysis of the impurity content of all the arsenic-containing wastes that were tested in the study.

Bacterial leaching of arsenic-containing ore (especially it is contains noble metals) is known to take place in flasks or leaching vats, under conditions of continuous agitation and aeration. The process is conducted at the indoor temperature (not less than 17-20 °C) [35-37].

We tried to make the process as simple as possible. For this purpose, we chose combined leaching, meaning the application of chemical extractants.

For the test were used the heterogenic bacteria *Thiobacillus ferrooxidans* (*T. ferrooxidans*) that had been preliminary adapted to arsenic and gold (Au). The nutrient medium of the bacteria consisted of nitrates, magnesium, chlorine, phosphorous, and iron (Fe). pH = 1.5-2.5, obtainable by sulfuric acid and R<sub>3</sub>. 3-4-7.5% arsenic samples were taken as the test specimens. The specimen-culture and R<sub>3</sub> ratio is as follows:

(1:5:0.5); 2) (1:5:0.3); 3) (1:5:0.25); 4) (1:5:0.2);

**Table 9.** Results of the proximate-quantitative analysis

Specimen	#1	#2	#3	#4	#5	#6	#7
Reg. #	290-S	291-S	292-S	293-S	294-S	295-S	296-S
Si %	>1	>1	>1	>1	>1	>1	>1
Al%	>1	>1	>1	>1	>1	>1	>1
Mg%	>1	>1	>1	>1	>1	>1	>1
Ca%	>1	0.06-0.1	>1	0.06-0.1	>1	0.06-0.1	0.1-0.3
Fe%	>1	>1	>1	>1	>1	0.5-1	>1
Mn%	0.1-0.3	0.1-0.3	0.1-0.3	0.1-0.3	0.1-0.3	0.01-0.03	0.1-0.3
Ni(g/t)	10-30	10-30	10-30	10-30	10-30	6-10	10-30
Co(g/t)	10-30	10-30	10-30	10-30	10-30	<6	6-10
Ti%	0.1-0.3	0.1-0.3	0.1-0.3	0.1-0.3	0.1-0.3	<0.001	0.1-0.3
V(g/t)	30-60	30-60	30-60	30-60	30-60	<6	30-60
Cr(g/t)	<30	<30	<30	<30	<30	30-60	30-60
Mo(g/t)	<1	<1	<1	<1	<1	<1	<1
W(g/t)	<100	<100	<100	100-300	<100	<100	<100
Cu(g/t)	30-60	30-60	30-60	30-60	30-60	30-60	30-60
Pb(g/t)	10-30	10	10-30	<10	<10	30-60	<10
Ag(g/t)	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Sn%	0.1-0.3	0.1-0.3	0.06-0.1	0.03-0.06	0.001-0.003	0.5-2	0.1-0.3
Bi(g/t)	<6	<6	<6	<6	<6	<6	<6
Sb(g/t)	<100	<100	<100	100-300	<100	<100	<100
Zn(g/t)	100-300	60-100	60-100	60-100	60-100	60-100	100-300
Cd(g/t)	<60	<60	<60	<60	<60	<60	<60
Ge(g/t)	<6	<6	<6	<6	<6	<6	<6
Ga(g/t)	10-30	10-30	10-30	10-30	10-30	<6	<6
In(g/t)	<6	<6	<6	<6	<6	<6	<6
Na%	>1	>1	>1	0.06-0.1	>1	0.01-0.03	0.3-0.6

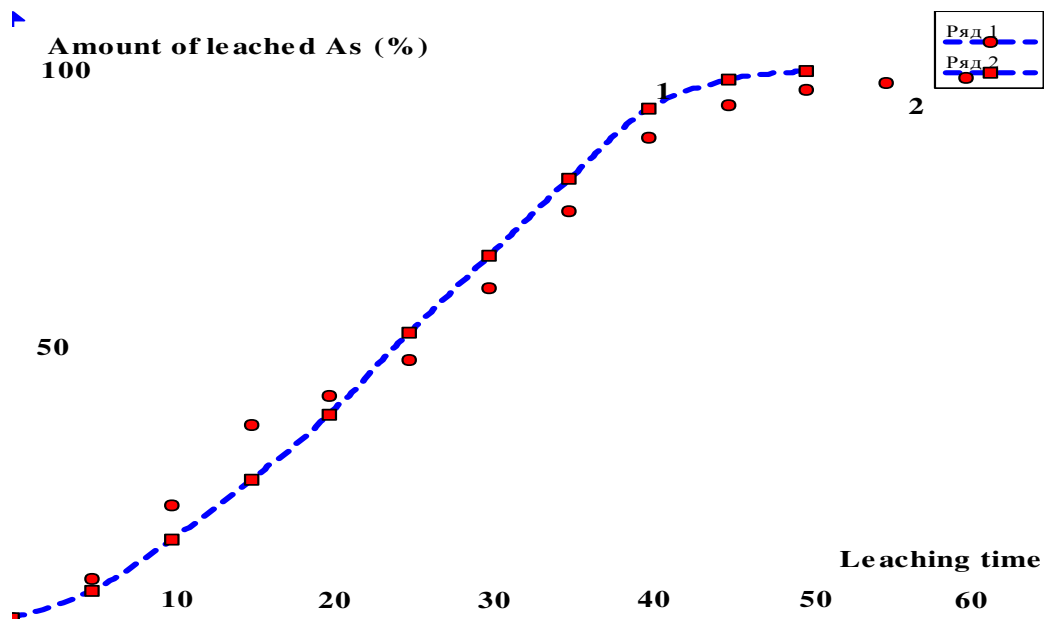
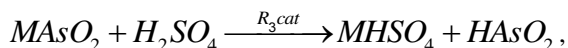


Figure 5. Bacterial-Chemical Leaching of realgar-orpiment wastes

The process takes place under conditions of continuous agitation, aeration and at 20-25° C temperature. If the waste is obtained as a result of annealing, arsenic will be then presented generally as oxide (Jinghong Zhang, *et al.* 2004), while metal arsenites (III) and arsenates (V) are easily and correspondingly oxidized.

The reaction medium is initially added with a R<sub>3</sub> mixture, which generally functions as a catalyst. In 60 hours the arsenic is completely leached from the specimen containing 7.12% of As [5]. At first, the process proceeds as follows:



where: *M* is the alkaline metal.

The R<sub>3</sub> catalyst greatly influenced the process in the following three directions, facilitating: (1) rapid bacterial disassimilation of the specimen; (2) its dissolving together with admixtures; and (3) the arsenic extraction.

It should be mentioned that the oxidation-recovery of the realgar-orpiment waste proceeds faster (48 hours) than that of the arsenopyrite waste (60 hours), as shown in Fig. 5.

Table 10. Charging of recoverable substances and product yield

№	Charging of recoverable substances					Yield of leached solution in dry residue %
	Arsenic-containing compound			Culture solution ml	Catalyst ml	
	Specimen	G	As content, %	( <i>T. ferrooxidans</i> )	R <sub>3</sub>	As
1	Production waste realgar-orpiment	100	7.50	500	50	96.5
2	Production waste realgar-orpiment	100	4.0	500	30	98.2
3	Arsenopyrite "tails"	100	3.0	500	25	93.8
4	'Arsenopyrite "tails"	100	2.6	500	20	94.6



As regards soils containing up to 1% arsenic, they do not require any combined action in the process. In 10 days the bacterial solution (where *T. ferrooxidans* is the nutrient medium) will leach arsenic in the insoluble form and decontaminate so soils from arsenic.

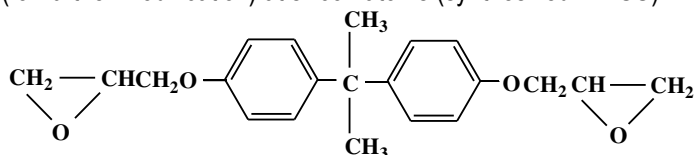
### 3.7. Polymer composites based on new carbofunctional oligosiloxane and biological active Adamantane – containing compounds for antibiocorrosive covers and conservers

Antibiocorrosive covers contain two components at least – biologically active compound and polymer matrix where the biologically active compound is dropped [39-44]. According to the literature data some polyfunctional heterochain organic polymers, such as polyurethane elastomers, polyurethane-acrylate, ionomers, etc., successfully has been used as a matrix for creation of antibiocorrosive covers from their solutions. The polymer matrix for the biocorrosive covers also may be obtained based on polyepoxide resins in mass in presence of the active diluents (Samakashvili 2006).

We chose the matrix-components for antibiocorrosion coatings (see below). We prepared more than 10 various samples antibiocorrosive coating composition of following three main types for plastics, wood and hard leather:

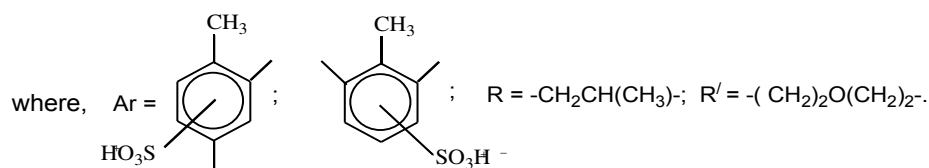
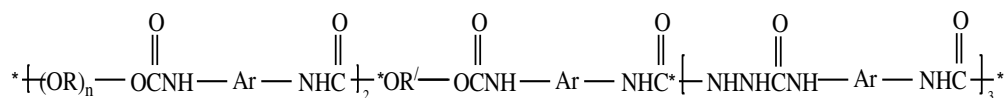
#### I. “Long-time active” composites:

a) Organic polyepoxide “ED-20” based on “Bisphenol A” + 5-10% silicon-organic epoxies with  $\text{CH}_2\text{Cl}$  (for further modification) at silicon atoms (synthesized in TSU):

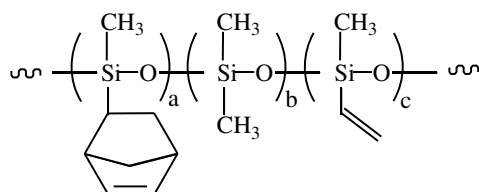


II. Polymer matrix, available to snuff for restoration, for example, museum exhibits (dissoluble in usual organic solvents):

1. a) Polyurethane PUSI synthesized:

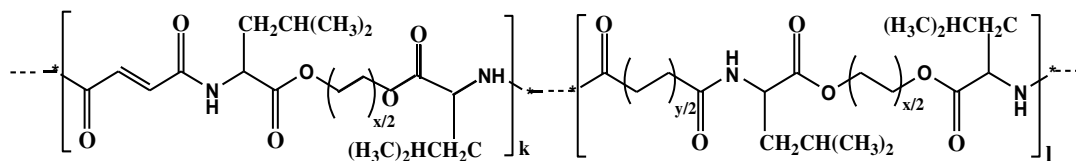


b) Polymer V1 + 3-5% polydimethylvinylsiloxane with dicyclopentadienyl radical at silicon atoms

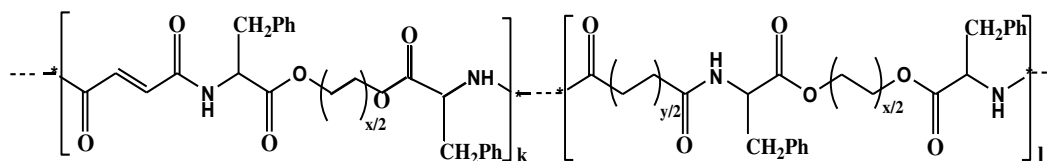


where,  $b \geq a > c$ .

III. "Short-time active" biodegradable composites based on polyesteramide (based on natural amino acids);



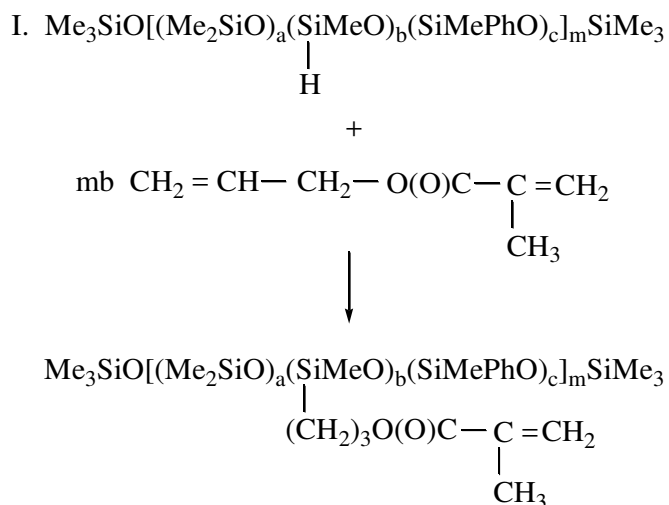
$$x=6; y=8; k+l=n$$

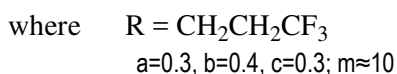
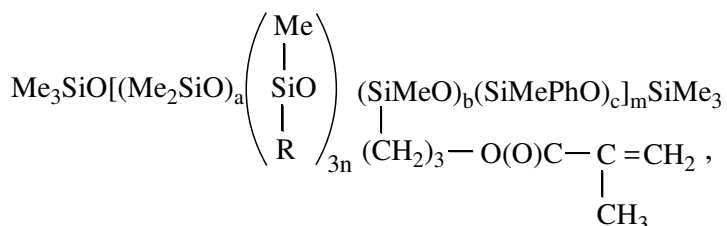
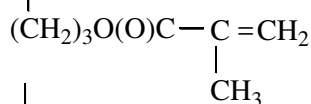


$$x=4,6; y=4,8; k+l=n$$

Application of the organic polyepoxide resins "ED-20" and "ED-26", also siliconorganic polymers with spatial dicyclopentadienyl groups for creation of the matrix for antibiocoorsive covers did not give satisfactory results. The obtained covers cracked during the exploitation and turn yellow.

More available from discussed matrix components is organic polyepoxide ED-20 or ED-26, (obtained based on "Bisphenol A") modified by new fluorine-containing carbofunctional oligo-organosiloxane with methacrylic groups at silicon atoms (MF-1-AMA-F<sub>3</sub>) by two stages according to the following scheme:





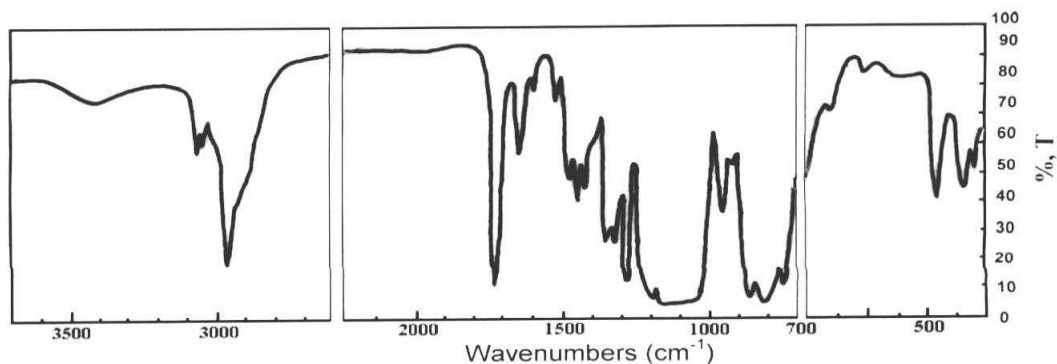
**Scheme 2.** General reaction scheme of obtaining of the oligomer MF-1-AMA-F<sub>3</sub>

On the first stage we synthesized the comb-type oligosiloxane with side allylmethacrylate fragment (Scheme 2). The process was controlled by determination of the content of active Si-H groups' in oligoorganohydridesiloxane by the method described in (Samakashvili 2006). During the hydrosilylation, a decrease of concentration of active Si-H groups with time was observed. Based on kinetical data of Si-H groups conversion (Samakashvili 2006) the reaction rate constant have been determined ( $k=0.13 \cdot 10^{-1} \text{ l.mol}^{-1}\text{c}^{-1}, T=70^\circ\text{C}$ ). The total reaction order equals to 2. The reaction proceeds at  $70^\circ\text{C}$  with conversion about 74-% (by determination of the active Si-H groups), while at  $90^\circ\text{C}$  it reaches about 83%. We established that at the same temperature ( $90^\circ\text{C}$ ) we reached the higher conversion of Si-H groups in case hydrosilylation MF-1 with AMA than with 12FA ( $\leq 77-78\%$ ).

The synthesized oligomers are vitreous liquids soluble in acetone, dioxane and ordinary aromatic-type organic solvents.

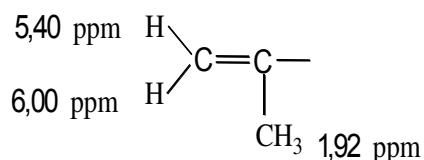
Structures and compositions of the oligomers were established by elemental analysis, IR and NMR spectral data.

In the IR spectrum (Fig. 6) of synthesized oligomer maximums of the absorptions ( $1040-1080 \text{ cm}^{-1}$ ,  $1440 \text{ cm}^{-1}$ ,  $1450 \text{ cm}^{-1}$ ,  $2930 \text{ cm}^{-1}$ ,  $2970 \text{ cm}^{-1}$ ,  $1605 \text{ cm}^{-1}$ ) related to the following groups Si-O-Si, Si-CH<sub>3</sub>, Si-C<sub>6</sub>H<sub>5</sub>, CH<sub>2</sub>, CH<sub>3</sub>, C<sub>6</sub>H<sub>5</sub> were observed. In IR spectra there were also observed the absorption maximums related to C=O, C-O-C and H<sub>2</sub>C=C groups ( $1735 \text{ cm}^{-1}$ ,  $1160 \text{ cm}^{-1}$ ,  $1650 \text{ cm}^{-1}$ ). In the IR spectrum there was not observed maximum of absorption for Si-H group.



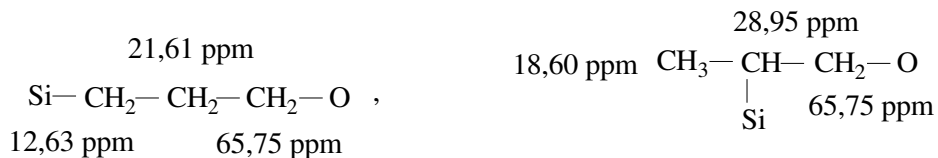
**Figure 6.** IR spectrum of adduct obtained from the interaction of MF-1 and AMA

In the  $^1\text{H}$  NMR spectrum of the hydrosilylation product (Figure 5a) there were identified the resonance signals with chemical shifts 1.92 ppm, 5.40 ppm and 6.00 ppm, related to the protons of the following group:

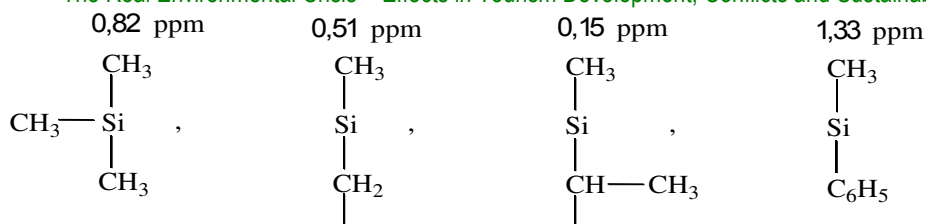


In the spectrum one can also observe the resonance signals of phenyl protons with chemical shifts in the range 7.0-7.6 ppm. There were also observed resonance signals with chemical shifts 1.2 ppm of the methylene groups, 1.1 ppm of the methyl groups and multiplet resonance signal in the range of 4-1.8 ppm related to the methine group. These data confirm formation of the fragments  $\text{CH}_2\text{-CH}_2$  ( $\alpha$ ) and  $\text{CH}_3\text{-CH}$  ( $\beta$ ) of feasible derivation of Markovnikov and anti-Markovnikov addition products.

In the  $^{13}\text{C}$  NMR spectrum (Figure 3b) of the same sample one can observe the presence of the resonance signal with the chemical shift 65.75 ppm related to the protons of the  $\text{OCH}_2$  group, and the resonance signal with the chemical shift 17.71 ppm related to the fragment of  $\text{CH}_3$  that indicates formation of both (Markovnikov and anti-Markovnikov) products:



In  $^{13}\text{C}$  NMR spectrum of the obtained oligomers we have identified four type  $\text{Si-CH}_3$ -contained groups, this is once again proves the presence of  $\alpha$  and  $\beta$  adducts (Markovnikov and anti-Markovnikov) <sup>15, 16</sup>.



By the ratio of integral intensity of correspond resonance signals we determined the ratio of  $\alpha$  and  $\beta$  adducts (39.13 : 60.87).

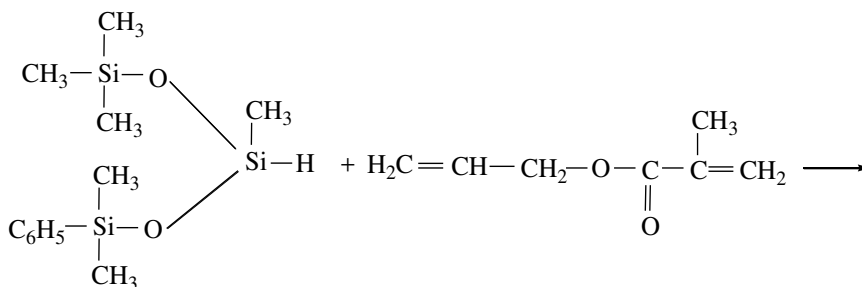
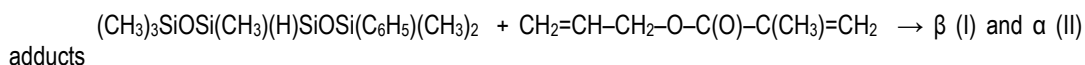
Semi empirical quantum methods used by us are simplified versions of the Hartree-Fock self-consistent field approach using empirical corrections derived from experimental data. These methods are usually referred to through acronyms encoding some of the underlying theoretical assumptions. We applied one of the most frequently used AM1 (Austin Model 1) methods. It is based on the neglect of differential diatomic overlap (NDDO) integral approximation. This approach belongs to the class of zero differential overlap (ZDO) methods, in which all two-electron integrals involving two-center charge distributions are neglected. If we base on the results of the arsenic analysis, the basic product content in the researched object makes up 98.7%. That correlates well with the chemical content of arsenic(III) sulfide obtained by direct synthesis.

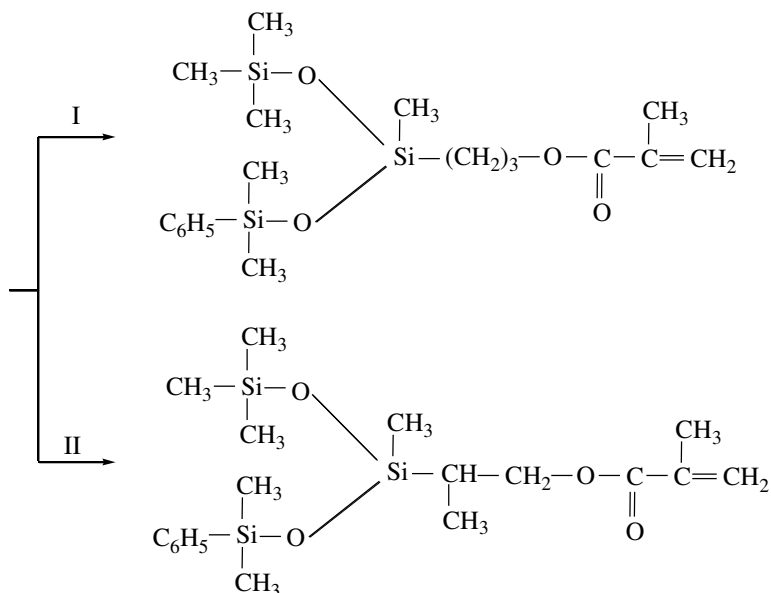
A number of additional approximations are made to speed up calculations and a number of parameterized corrections are made for corrections of the approximations in the quantum-mechanical model. For AM1, the parameterization performed so that we obtain enthalpies of formation  $\Delta H_f$  instead of total enthalpies, as a function of the distance R–C–Si. The calculations provide us also with P1 values which represent bond orders (Allinger 1977).

We have performed calculations using a semiempirical AM1 method for modeling reaction between of oligomethylphenylhydridesiloxane (MF-1) to AMA using software Chem3D. Such calculations for polymethylhydridesiloxane and AMA are not doable since the software does not produce reliable results for systems with more than 100 atoms. Necessarily, numerical values for the model reaction will be different than for the polymers studied experimentally but will provide better understanding of the experimental results (Scheme 2).

We consider the hydrosilylation of  $(\text{CH}_3)_3\text{SiOSi}(\text{CH}_3)(\text{H})\text{SiOSi}(\text{C}_6\text{H}_5)(\text{CH}_3)_2$  (MF-1) with AMA in view of the anti-Markovnikov and Markovnikov rules. According to the model reactions compounds I and II will be obtained (Scheme 3).

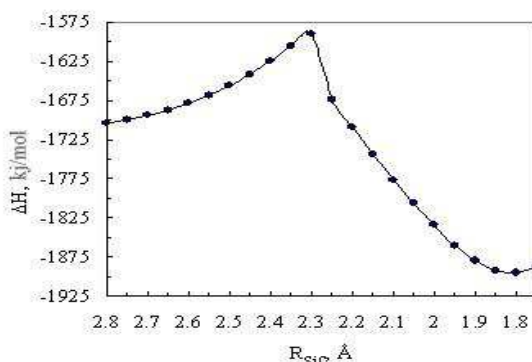
The hydrosilylation reaction is considered through the following model reaction:





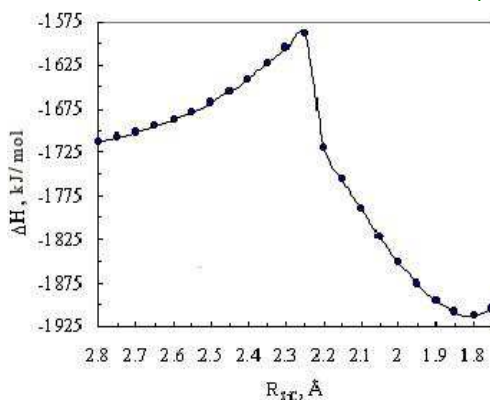
**Scheme 3.** Model system for the calculation of  $\Delta\Delta H^\ddagger$  and  $\Delta\Delta H$  for products of hydrosilylation of MF-1 with AMA

The activation energy of  $\alpha$ -adduct is  $\Delta\Delta H^\ddagger=124.8$  kJ/mole ( $R_{SiC} = 2.30$  Å), and for  $\beta$  adduct is  $\Delta\Delta H^\ddagger=114.4$  kJ/mole ( $R_{SiC} = 2.25$  Å). In the both cases the combination process is exothermic ( $\Delta\Delta H = -199.3$  kJ/mole and  $\Delta\Delta H = -191.2$  kJ/mole respectively). The low value of activation energy of  $\beta$ -product indicates the superiority of performing the reaction in this direction. Compare now  $\Delta H_f$  values for compounds of addition taking also into account Figures 7 and 8. Clearly, hydrosilylation reaction of  $(CH_3)_3SiOSi(CH_3)(H)SiOSi(C_6H_5)(CH_3)_2$  to AMA is energetically more favourable according to the anti-Markovnikov rule behind to Markovnikov rule. This result is in good agreement with NMR spectral data.



**Figure 7.** The dependence of enthalpy ( $\Delta H$ ) on the reaction coordinate ( $R_{SiC}$ ) for  $\alpha$ -adduct

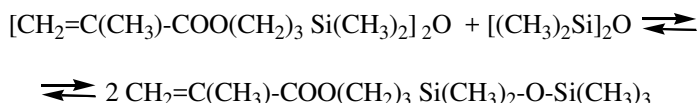




**Figure 8.** The dependence of enthalpy ( $\Delta H$ ) on the reaction coordinate ( $R_{sic}$ ) for adduct

On the second stage we have carried out the catalytic cooligomerization reaction of obtained methacrylate with trimethyltri(trifluorinepropylene)cyclotrisiloxane in toluene at 80°C, in presence of sulfocationit “CU 23”, 1.5-2 mass % (It is manufactured based on copolymer of divinylbenzene with styrene) and hydroquinone (inhibitor) (1 mass %) (Lekishvili *et al.* 2009).

Investigation of the model reaction (Scheme 4) by CLC method<sup>18</sup> showed that this reaction, in the conditions of the reaction of the cooligomerization, is characterized by the establishment of the equilibrium at room temperature (25°C) during 8 hours. The conversion of the hexametyldisiloxane (HMDS) reaches 50%<sup>20</sup>. By an increase of the temperature till 70°C, the time for the establishment of the equilibrium decrease till 2.8 hrs.



**Scheme 4.** General scheme of the model reaction

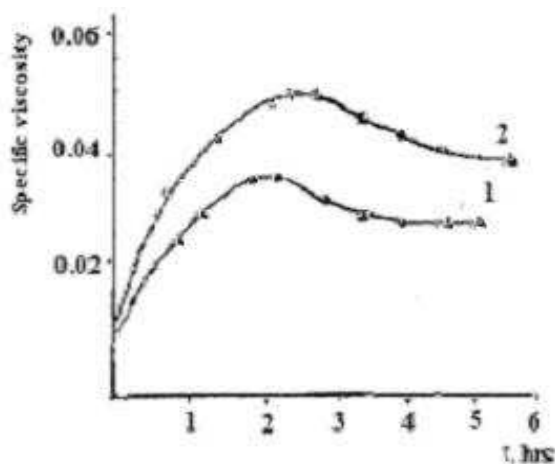
The value of the specific viscosity of the product of cooligomerization depends on the molar ratio of MF-1–AMA and cyclosiloxane (Table 8) and on the reaction temperature. From the figure 8 it is evident that the curves of dependence of the value of specific viscosity  $\eta_{sp}$  on the time have an extreme character: in the beginning, the  $\eta_{sp}$  reaches the maximal value for 2.5-3 hours at the organosiloxane conversion of 80-85%, increases and the value is kept constant for the obtained oligomers 5.5-6.0 hrs. The  $\eta_{sp}$  decreases till certain constant value (Fig. 9, Table 11).

It must be noted that the value of the specific viscosity of the products of cooligo-merization, in comparison with analogical systems<sup>14</sup>, increases slowly, what may be connected with the increasing of the strict factor at the silicon atoms in MF-1-AMA.

**Table 11.** The reaction conditions of cooligomerization of MF-AMA and F<sub>3</sub>, and some characteristics of reaction products

#	Initial substances molar ratio		T, °C	Duration of the reaction, hr	$\eta_{\text{spec}}$	$M_{\eta}^*$
	MF-AMA	F <sub>3</sub>				
1	1	4	80	6	0,035	2523
2	1	6	80	6	0,028	1784

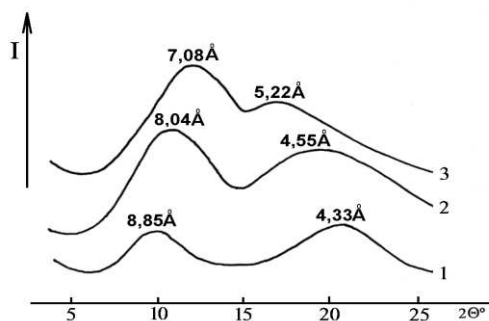
$$^*)M_{\eta}=[\eta \cdot 5000]^{1.515}$$



**Figure 9.** Dependence of the value of specific viscosity of cooligomerization products of MF-1-AMA with F<sub>3</sub> (1) at the 80°C

The obtained copolymers are white viscous products soluble in ordinary organic solvents (toluene, dimethylformamide). The composition and structure of synthesized cooligomers were studied based on data elemental analysis and IR spectra. After degassing ( $t=373-393\text{K}$ ,  $P_{\text{resid.}}=13-14\text{ MPa}$ ) of adducts the IR investigation was performed. In the IR spectrum the characteristic maximums of the absorption ( $1040-1080\text{ cm}^{-1}$ ,  $1440\text{ cm}^{-1}$ ,  $1450\text{ cm}^{-1}$ ,  $1720\text{ cm}^{-1}$ ,  $1645\text{ cm}^{-1}$ ,  $2970\text{ cm}^{-1}$ ,  $1600\text{ cm}^{-1}$ ) of Si-O-Si, Si-CH<sub>3</sub>, Si-C<sub>6</sub>H<sub>5</sub>, C=O, C=C, CH<sub>3</sub>, C<sub>6</sub>H<sub>5</sub> groups and ( $1170\text{ cm}^{-1}$ ,  $1270\text{ cm}^{-1}$ ) also maximums of the absorption to C-F(CF<sub>3</sub>) groups were observed <sup>9</sup>.

We have determined for synthesized oligomers wide-angle X-ray scattering (WAXS). Figure 10 shows that the oligomers are amorphous one-phase systems. Diffraction patterns display two maxima. First  $2\theta^0 \approx 10.5$  corresponds to the maximum of the inter-chain distance  $d_1 \approx 8.85\text{ \AA}$  while the second ( $2\theta^0 \approx 21$ ) corresponds to  $d_2 \approx 4.33\text{ \AA}$  which characterizes both intra-molecular and inter-chain interactions.



**Figure 10.** Wide-angle X-ray patterns of synthesized oligomers:  
 1. MF-AMA/F<sub>3</sub> (1:6), 2. MF-AMA (1:1), 3. MF-1-13FA (1:1)

By differential-scanning calorimetric (DSC) studies we determined that synthesized oligomers are amorphous one-phase systems (Figure 11). From analysis of DCS curves is shown that the incorporation of perfluoromethacrylic radical in the chain of oligomethylphenylsiloxane (MF-1) modified with allylmethacrylate, results to the rise of the transition temperature ( $T_g$ ) on a 19°C.

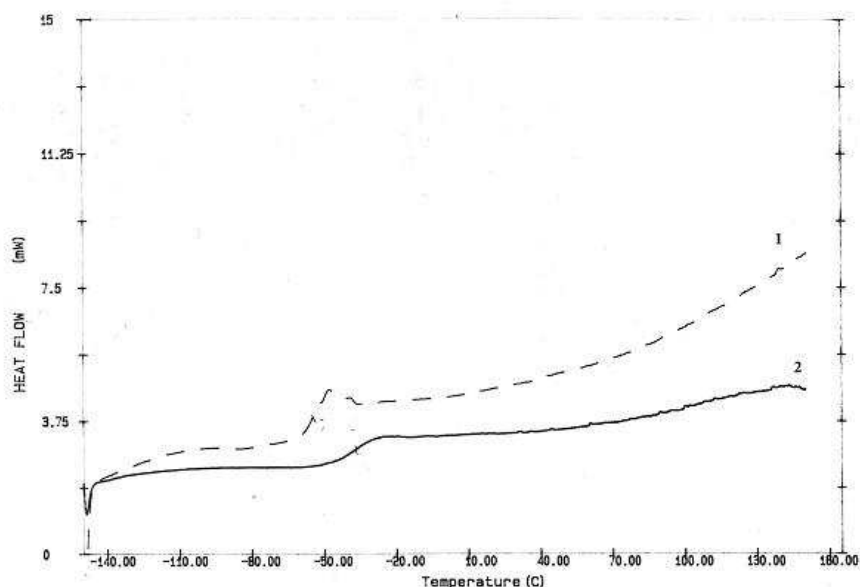
We also fabricated new anticorrosion coatings based on new matrices (see below).

Preliminary we tested the bactericidal and fungicidal activity of synthesized arsenic and stibium-containing complex compounds (Scheme 5, 1-2 3, 4); synthesized based on arsenic industrial waste transformation products.

1.  $[(C_6H_{11})_2As C_6H_5CH_2J]_2[ZnBr_4]$
2.  $[(nC_3H_7)_3As(CH_2)]_2[CdJ_4]$
3.  $NiCl_2 \cdot 2Li, [Li_4 = CH_3CONH(C_6H_4)AsO(OH)_2]$
4.  $[(C_6H_5)_3As(CH_2)]_3SbS_4$

(Scheme 5)

To this target we have applied the test-microorganisms – *Pectobacterium aroideae*, *Fusarium arenaceum*, *Autinomyces Griseus* and *Fusarium proliferate*. Following concentrations of substances: (g/l) 1.0; 0.1; 0.01 have been used in experiments by us. Bactericidal properties were determined according to the method described in Markarashvili *et al.* 2006.



**Figure 11.** DSC curves of oligomers: 1.- MF-AMA (1:1); 2.- MF-1-AMA-F<sub>3</sub> (1:1)

The test results showed that the synthesized compounds 3 and 4 (Scheme 4) have revealed selectively bactericidal properties and have suppressed the development of research cultures. The compounds 3 and 4 especially actively have an influence upon a bacterium *Pectobacterium aroideae*, which have strike the melons and gourds and provoke rot, - halo of inhibition in a case of compound 2 is 2 and 5 mm by concentration 0.1 and 0.01 g/l correspondingly, and 6 and 2 mm in a case of compound 3 by concentration 1.0 and 0.01 g/l correspondingly.

It must be noted that the compounds 3 and 4 more actively have an effect by concentration 0.01 g/l on *Pectobacterium aroideae* and *Act. Griseus* (producer of antibiotic), halo of inhibition is 1 and 3 mm correspondingly. It must note that the bioactivity of the initial nitroanilides is less then bioactivity of their complex compounds. For example, in case of *Fusarium arenaceum*, halo of inhibition for 4-(p-chlorophenoxy)-2-nitro-3-chloro-N-(1-adamantoyl)anilide (Scheme 4, 1) is 1 mm at concentration 0.1g/l correspondingly.

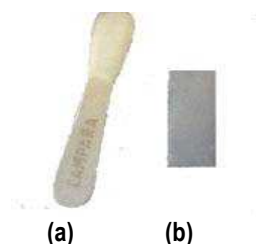
We have prepared antibiocoorsive covers based on synthesized bioactive compounds. Before coating on the goods' surfaces (plastics, wood, etc.) for protection, to the synthesized compounds (nitroanilides or complex compounds based on them – bioactive substances ( $\leq 3\%$ ), oligoorganosiloxane MF-AMA (modifier for matrix compound  $\leq 10\%$ ) in composition with the “ED-20” (modified by siliconorganic oligomer with metacrylic groups at silicon atoms. and hardening agent – hexamethylenediamine ( $\leq 5\%$ )). Later the producing thin layers on the surface of the selected material (lead, plastic, etc.) were holding on the air for 24-48 hours at room temperature. After hardening on the surface it was produced homogenous, smooth, thick mechanically stable protective layer. It must note that the produced compositions are available and their production is technologically simple.

Practically for researches some physical properties antibiocoorsion coatings films we formed on the teflon surfaces from solutions in usual organic solvents.

Preliminary researches show that the obtained antibiocoorsion coatings are transparent, smooth and visual homogenate with good adhesion on various surfaces (plastics, wood, hard leather). Study of the Stability during thermal aging (40-50° on the air) show that the antibiocoorsion coating films did not changed during 300hrs. Their water absorption did not rank over 0.03% and

have minimal value for anticorrosion coating films based on organosilicon epoxide matrix and siliconorganic oligomers MF-1 in comparison with the other coating films.

The basic properties of protective layers (homogeneity, viscosity, compatibility of polymer matrix components with bioactive compounds), physical and chemical characteristics (water absorption  $\leq 0.2\%$ ), and adhesion strength  $\geq 4.0\text{-MPa}$ ) are in compliance with the compositions of protective layers of objective types [49, 50].



**Figure 12.** Anticorrosive covers based on arsonium triiodides and siliconorganic matrix based on MF-1 for wood (a, higher part of the sample) and plastic (b)

The preliminary testing of obtained bioactive composites showed that they may be recommended as: a) protective covers with multivectorial application (film materials and impregnating compositions) stable to biocorrosion; b) materials with antimycotic properties for prophylaxis and treatment of mycosis; c) biologically active polymer materials for crops protection and d) for human protection during its contact with microorganisms.

The solve of such projects will speed to integration of Georgia in European democratic structures and search new work places that will improve the life level of South European region population.

#### 4. Conclusions

On the basis of arsenic production industrial waste and their transformation products:

We separated the natural forms of arsenic and stibium oxides by transformation of the Georgian region industrial waste of arsenic production. We studied of the process of separation.

We studied of the possibility of producing arsenic(III) sulfide from the industrial residuals of pyrometallurgical processing of nonferrous and precious metals ores we considered.

Based on arsenic industrial waste we synthesized of arsenic and stibium chlorides, alkoxydes and complex compounds for preparation of new antibacterial sources and fungicides for protection of plants, anticorrosive covers for various synthetic, artificial and natural materials (leather, wood, and plastics).

Synthesize arsenic-containing chemically active compounds alkoxydes, alkylarychlorids, alkylarylarsonium salts and bioactive complex compounds on basis of the arsenic industrial waste.

Investigation of diphenylaminochlorarsine, obtained bioactive chelates and cationic-anionic complexes of d-metals containing arsenic and stibium to use the former in multi-vector anticorrosive covers and anti-microbe conservers; manufacturing and testing new cheap means for protection of archeological items, museum exhibits from mycosis and for protection of plants from micopathogenic microorganisms; investigation of the prospective pharmacological effects of obtained bioactive compounds;

From industrial waste of pirometalurgy production of arsenic will obtain: White arsenic with high cleanness for use in pharmacopoeia.

We shall obtain new economic compounds and materials based on them and fulfil the technical order of business, definition of possibilities of creation of joint enterprises with limited liability.

Success in solution of the aforementioned tasks, on the basis of industrial wastes in Georgia (e.g., those of arsenic industry secondary mineral resources) we could produce new low-cost functional organic-inorganic compounds and materials with specific properties. Likewise, we can manufacture organic-inorganic composite materials as relatively cheap alternatives in comparison with the existed;

One should note that the solution of these problems would result in that of many ecologic problems.

## 5. Acknowledgment:

*Authors thank Rustaveli National Scientific Foundation (Georgia) to financial support and Dr. E. Markarashvili and Dr. E. Chkhaidze for help in synthesis some matrix component for antibiocoorrosion coatings.*

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# THE IMPACT OF TOURISM ON ECONOMIC DEVELOPMENT

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## Abstract:

*Tourism is an economic activity which directly and indirectly affects the economic development of a country. Analyses of studies are the best indicator of how tourism affects the economic development of regions and districts of a country. To develop tourism in each country there are some preconditions. Countries with potential in tourism must make it functional, part of tourist offer. In this way tourism development affects the establishment of economic development by raising the local GDP and changing the physiognomy of the landscape of different regions and tourist areas.*

**Keywords** - tourism, economic development, economic effects, the sectors of tourism, GDP.

## 1. Introduction

Tourism as an economic activity creates income from visitors. Visitors are seeking a range of services which should be in the service of their claims. Much of the workforce can participate in different ways in function of tourist services. Especially, the development of tourism in developing countries can provide economic impetus from various activities; such as supply of various local products, use of accommodation, use of transport, the development of tourism operators, etc. Role of the local businesses and public organizations is related to tourism and has economic impacts at the national, state and local level. Every country or area, where tourism is developed, as part of tourist offer is the use of natural and anthropogenic resources that are associated with the income of that country or community. Tourism has a multiplicative effect because the sectors in a community who benefit from tourism belong to a considerable number of economic activities.

## 2. Impact of tourism and its effects on economic development

The impact of tourism on economic development may use the appropriate methodology in order to search results, which is the contribution of tourism to economic development activities in the region or even beyond. On the basis of economic analysis of the role of costs associated with tourism activities, is to identify changes in sales, tax revenues and jobs that are associated with tourism. To study the economic impact analysis should assess the economic contribution of tourism to the economy of a country. Should pose the question of how this area is visited by tourists in order to have access to guidance. It needs to know which products are sold too many local businesses, from tourism activity. It would be inappropriate to analyze how much is the amount of revenue which are generated by tourism for families and businesses in the area. This will facilitate us to understand the effect of tourism on economic development activities. Then it follows that we will have to clear that much work can support the tourism sector, for that part. But the significance will be how much is the amount of tax revenue generated from tourism for the country in order to support the state. All analysis highlights the relationship between sectors of the economy and provides estimates of changes that occur in an economy because of some existing or proposed actions. Economic impacts of tourism can change the levels of tourist activity, expenses, and related economic activity between them.

### **3. As influences tourism in economic development**

Tourism has varied impact on economic development. Tourists contribute to the sale of products, realization of gains for the population, in employment, in income tax and in general that is the earning of a country or a region. With direct effects occur within the sectors of tourism such as accommodation, restaurants, transportation, entertainment and retail. The economic impact of tourism analysis focuses on changes in sales, income and employment in the region where tourist activity is developed. Better benefits realized from the impact of tourism. If a country pulls 100 tourists a day then if one day each tourist spends from 10 Euro, then within a day in that area will be spent by tourists 1000 Euro for day, or if calculated for a year then will be carried 365,000 Euro only with this figure, this is just one of the simplest examples. In this way the region or country will gather a good income that will be distributed at the event yet as housing, restaurants, entertainment, retail, etc... On the other hand there are some categories of economic impacts are typically not covered in the economic impact and assessments, at least not directly. As an example we can change the price. Sometimes it can affect the cost of house prices and in retail in that area, especially in certain seasons. Changes in quality and quantity of goods and services expressed the impact of tourism in tourist seasons. Further changes in property and other taxes such as taxes to cover the cost of local services may be higher or lower depending on the tourist seasons. The role of tourism in economic development is manifold. Benefit from tourism and other businesses that work supply good and services to tourism businesses. The impact of tourism to economic development has direct and indirect role. These impacts can be measured GDP, or sales, income, employment, or value added. Direct effects are associated with changes in production immediate effects of changes in tourism expenditure. With the increasing number of tourists who are placed in accommodation units will directly affect the realization of revenues in the hotel sector.

All enter the direct effects of tourist spending.

The indirect effects are as varied supply of different products, the change in sales, jobs, and earnings in the industry and we supply. How tourism businesses supply make the effect of brace, which eventually connected with the hotels in varying degrees in many other sectors in the country but also beyond. The effects of tourism are different from economic activities arising from expenditure and income earned them directly or indirectly as a result of tourism spending. An example would be to get an accommodation facility and employees who are supported economically from tourism who spend their income in the region in which they live. In this way the impact of tourism is crucial for economic development and function overall economy. In considering the economic aspects respectively by increasing the number of tourist trips added to the number of bidder's tourist services, from which more and more visible benefits that bring tourist flows. If analyzed before it can result, watching historically always result in more tourist activities tourist consumption, which create economic effect which affect the establishment of national economies of many countries. Effects and economic importance of tourism is multi-dimensional and can be led to establish some priorities for the economy, using the potentials available. Tourism makes it possible to valorizations of natural goods such as air, water, climate, and landscape attractions etc, which all receive the economic value. In developed regions without which give importance to tourism development where conditions for visits by tourists, create market for local produce which products will not reach the market. Tourism can rightly be called a specific export but also import foreign currencies that matter multiple local economy in tourist areas. Sometimes we get ready for tourism as it is a branch which affects economic development, which is not absolutely accurate. This presents even more difficulty, and all have their negative effects, especially in areas that caused environmental pollution and environmental degradation. But nevertheless each country which is oriented to the development of tourism should also prepare the best and most effective for this activity which has to function in other activities related to its effect to be positive without prejudice

surrounding environment. The effect and importance of the tourist is his way of achieving the selected country resort in which he begins to spend its money in that country. In some cases, tourists may be presented as a buyer of everything that it makes available to providers individually.

We stay tourist sites bidder who, by visitors expect to buy their goods. All this is as a benchmark of research of the economic effects of tourism where tourist spending, the share of consumption which is earmarked for travel and stay outside the location of permanent residence in order to rest, leisure and recreation. Tourists to meet the wishes of the people are forced to travel in selected countries, in which the use of any means of transport to travel. This means that tourism is related to traffic, which is one of the basic sectors and economic importance, which absorbs a portion of funds allocated for tourist consumption. With the arrival of the visitor at a certain location it becomes a user of hotel services, food and beverages. In this way absorbs hotel is one of the biggest tourist consumption. Greater importance is the tourism agencies, which are in contact with the spenders in the organization of trips, during formation of the arrangements and delivery of various services. Each visitor directly to the so-called budget tourist spends in these branches: hotels, traffic, commerce, travel agencies and branches and other tourist activities. Based on studies and analysis can be concluded that tourism can not be identified in only one economic branch, since it constitutes a component of activities and branches of the economy. Tourism also has implications for infrastructure and superstructure frequency, where without can not imagine that tourist flows. While trade is specific economic activity, maid of honor participants intensively introduce tourist offer. With tourism in total means of economic and non economic activities which, interact in a fair and oblique, that their activities enable the operation of the tourism market. According to its tourism can look in the broad sense and narrow. In the broad sense that includes everything which participates in any way in shaping the activities which were dedicated tourists. In addition to the four activities mentioned above here they are part of the agriculture, forestry, food industry, construction, extraction industry, education, health, etc. Strictly observe tourism through two economic activities which are based tourism activities: The hotel and tourist agencies. According to the results that the hotel is the basis on which the activity raised tourist resort because it is forced to use the service of accommodation, food and beverages. It is important that the value of the benefit of the total tourist spending of tourists have divided government from foreign tourists, because in essence the impact of these categories of consumers in national economies is different. Tourist's resident dedicated the expenditure of tourist needs to spend within his country. In these kinds of tourists do not increase nor decrease the national income Tourist consumption of the local Tourism and its impact on economy is important because it represents a considerable source of currency value and so we have been exporting activity itself, which its revenues of embodies the "Invisible export" or as it is called "Export in the country of the event". Beautiful big advantages are that tourism has in relation to other exporting activities, which are directly involved in international exchange of goods. This created great advantage which is reflected by the fact that tourists travelling tourist market (customer), in this case the customer arrives at the place of consumption, thereby tourist goods but also services consumed in tourist destination only in the presence of tourist-consumer.

#### 4. Conclusion

Multiplicative effect of tourism is because the sectors in a community who benefit from tourism belong to a considerable number of economic activates. Multiplicative effect of tourism is because the sectors in a community who benefit from tourism belong to a considerable number of economic activities.

Effect of Tourism is mainly oriented tourist consumption. Tourism affects positive, revenue growth and living standards, improves the local economy, increase employment opportunities, improves the level of investment, develop infrastructure, increase tax revenues, improve

infrastructure, public services, improving transport infrastructure, increase opportunities market, and creates new opportunities for business. While the negative aspects of tourism effects are small, raises the prices of goods, etc. The cost of living increases. Countries and areas different from their orientation in the effort have changed the physiognomy of the landscape today are attractive places which are used for purposes of rest and recreation. These countries modern infrastructure but also are attractive areas for visitors. The impact of tourism in economic development is important from the tourism multi-dimensional foreign currency creates for the local population but also in setting up local GDP. Impact of Tourism in the economy according to research analysis and forecasting will be tourist turnover growth and income to the tourist places which will affect the overall economic development.

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The First Online International Conference on  
“The Real Environmental Crisis – Effects in Tourism Development, Conflicts and Sustainability”

# **TOURISM AS AN OPPORTUNITY FOR ECONOMIC DEVELOPMENT, QUALITY MANAGEMENT REQUISITE FOR SUSTAINABILITY**

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## **Abstract:**

*Now day's tourism is treated as an economical activity with a constant growth all over the world, this is also expected for Kosovo's tourism and nearby countries for coming periods of time. In some developed countries tourism is treated as an important exporter and in meantime as an absorber of labour force and this branch is important for softening unemployment. Management with total quality in tourist industry and catering has its own specifics. A big attention should be paid to standards that have to do with quality and insured goods supplied to hotels, and those provided in tourism. Quality care is being placed in the first place, in wholesale of successful tourist enterprises. Here it should be noticed the fact that there is a liaison between the quality, consumers pleasure and consumers loyalty.*

**Key words:** tourism, quality, standards, management, development.

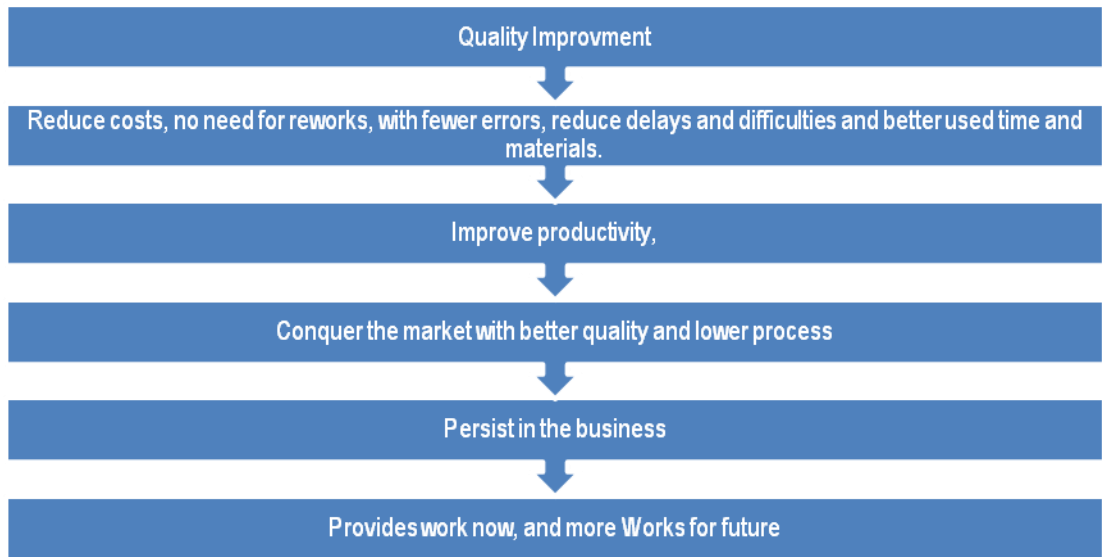
## **1. Introduction**

Learning from advances of the countries of region Kosovo can make a bigger progression to increase tourist number not just during the main season of tourism (counting 3 months of summer) but also during the rest of the year. In this project total quality is described in tourism and hospitality. Management of total quality is one of the managing models that apply in business of enterprises in order of application, maintenance and progression of service quality and tourist product also. We can conclude that tourism development in Kosovo, in general it was not concentrated, due to distribution of tourism location and destination everywhere, so there is dispersion all over the country that results with socio-economic factors in different regions. Whether it is better that tourism development should be concentrated or distributed in geographic aspect, at the level of theory it cannot be given a final conclusion. This is because each shape, even the one when tourism and hospitality development becomes more and faster in some regions than others, or when tourism and hospitality development is concentrated in regions all around at the same time, or at the country level its has comparative advantages and disadvantages, so we suggest that reasoning of concentrated development or spread should be verified by concrete cases based also in socio-economic targets which we want to achieve with this development. Starting from the description of tourism and its quality we pass to standards that are applied in hospitality and tourism, variety and types of quality and its development, contributing the growth of business.

The future of the hospitality is in small hotels that will be the pillar of tourism development. However what should be suggested is caution to safety standards and health maintenance of guests in hotels. A great attention should be paid to standards dealing with quality and safety of goods supplied in hotels. Certainly that conclusion is, that tourism and hospitality to the Kosovo have a perspective, but this should be achieved by efforts to reach standards and total quality, and the most important is that once they are achieved they should be maintained and consistently introduced to innovations. In project we used deductive and inductive methods.

## 2. Quality management in tourism

Many individuals have contributed on the analysis and implementation of quality management, among them is Edward W. Deming, J.M.Juran, and F.B. Krosby. Philosophy of quality management of Deming who is mentioned constantly when fundamental principles of quality management are stressed. It is known the theory of “Chain Reaction” of Deming which states that the highest quality leads to a higher productivity which in turn leads to a long-term competitive strength (Nakuci 2009).



**Figure 1.** Chain Reaction of Deming

Whereas Juran, J.M. centralizes the quality issue in three major aspects called as “The Trilogy of Quality”: planning of quality, control of quality, and improvement of quality. Therefore this author considers the management of quality of primary importance as a management component in all enterprises (Nakuci, 2009).

Being a service activity, tourism contributes to life quality because it makes people happier and healthier in general. The management of total quality in the tourist industry, with its branch catering, has its own specifics, being also related to the characteristics of provided services in tourism alongside with the products in other economical activities.

The characteristics of tourist services are: inviolability (immaterial), short-term, isochronous, diversity. Except these general characteristics listed above, the tourist and catering services have their own specific features, considering the diversity of the tourist product provided at present, but also there is the diversity of those who on the other side use the tourist product.

The tourist product is defined as a set of heterogeneous products and services, such as hotels, restaurants, market, transport, tourist attractions, cultural and historical inheritance, etc. whereas the local population and the economy of the country are considered factors too. All such products and services, defined as tourist products, must be subject to the aim of achieving higher quality because their users are increasingly being refined in their demands and increase their demand for higher quality.

Therefore, those who deal with this activity are always trying to get to satisfy the demand, but also to exceed the expectations of tourists, because they are aware that there is competition in this market. Indeed, quality is becoming the main and decisive factor for efficient competition of

enterprises in the tourist market. The users, costumers, or briefly defined as tourists, want to receive quality, so the enterprises with their tourist offers manage with quality and have to control it continuously. It is normal to learn from leading countries in quality management such as USA, Sweden, and Switzerland.

The meaning of the word quality now days is multiple because it is composed of many elements, which come out from various qualities of different goods and services, activities, use benefits and values, the manner of use, the significance it is given by the users, etc. This quality of goods and services is formed in all phases of their life cycles, beginning from the researches and developments up to their exploitation. All the phases during which the product quality is formed are introduced as the components of structure of the goods or the service itself, and they are known in theory as functions of quality. Each quality functions represent a composed entirety which is built of more specific units, and which impacts in the quality of that good or service. All the functions are interrelated with each other and often there is no difference or limit between them, and at the same time they are all under the impact of internal and external factors.

The elements of the quality of goods or a service, such as wine, are: colour, clearness, taste and flavour, whereas the elements to ascertain the quality of a restaurant could be: the architecture of the building, hospitality, table, the menu, service and personnel, food, drinks, the bill, and behaviour with guests. Therefore each of the elements forms a part of the overall quality of the wine and restaurant. This resulted on ranking the quality and leads to the competition between companies trying to be the best, the first and the biggest, aiming to create a competitive advantage within the market where they operate. Whereas the ranking method and the way of expressing the level of quality may be different, one of those could be: counting the number of stars, numbers or different figures. Also, the price plays a role in the quality level, whether it is expensive or cheap it is an indicator of high or low quality. As far as the quality is concerned, it is enabled by identifying the brand of the Hotel (Holiday Inn) or the air company (Austrian).

Now days, the quality could be identified based on revenues, as one of the economic targets of the enterprises, including the adoption of a management system with the total quality and it is estimated to be reasonable and successful if they manage to boost their revenues and decrease expenditures which results in profit generation. Regardless of whether we are dealing with the manufacturing or service enterprise, the quality has to be always in the main focus of those who design the business policies of an enterprise. This is because the quality is associated with many product elements that aim to satisfy customers' needs. If we take the case of catering services, or catering tourist product, than we are aware about the important role of users or tourists about the tourist offer, because in this case they are treated as an integral part of that certain tourist product. Out of these assessments, we can estimate that for tourist enterprises the user or tourist is the most valuable part of the company's assets and from this it results that the company's strategic orientation for the quality of offer will bring them a competitive advantage in the market.

The quality of tourist and catering product must be advanced as result of adoption towards the changes which increasingly are more dynamic as far as the demand is concerned. A large differentiation is happening between market segments, and such quality will help to find the appropriate position within the market. A clear position of Kosovo tourist product as a whole as well as in parts will enable a definition of all those segments during the process of strategic management within the tourism industry. Kosovo tourism during the recent period is striving to follow-up tourism development trends in the region as well as the global level developments. Having into account the role of tourism and the environment in which the tourist industry is located, it is heading towards stable markets, but also towards new ways of provision of supply, which requires creation of new tourist products. When dealing with stable market in such cases everything has to be done to

enhance the quality level of Kosovo tourist products in terms of overall product as well as for its components.

The highest quality of the existing location requires focusing towards users or tourists of certain segments to whom it is necessary to provide a package containing units that are related to the system which would create the certain product. An example for this could be the relation of destinations located in Dukagjini area (Dukagjini Plain) in an arrangement that would reflect the highest existing quality. In other destinations that are usually smaller and have a limited capacity to accept a smaller number of users or tourists, in such cases the tourist product can be associated with the new forms of tourism such eco tourism, which is correlated with the tradition and folklore, new products from the rural areas and naturally preserved beauty sites.

New destinations themselves create new tourist products, which in order to meet the sustainable principles of the product need to be subject of several phases that form a part of it, and which requires a continuous attention towards the quality. As a first plan derive opportunities for accommodation, meal and activities not included in the package. In this case it is very important that a large number of those activities that constitute "costs not included in the package" which puts an attention to its structure including the gastronomy, hospitality, entertainment, which will largely be a result of possibilities of that certain destination.

Whereas in the second plan takes place the infrastructure of the tourist offer, which needs to be uniform throughout Kosovo. This applies to the roads, water supply and wastewater, power supply which serves to facilitate the arrival and provides pleasure to tourists during their stay, and will create an opportunity to such tourists to not force them in changing their lifestyle and habits. Construction of sport areas, different ethnological, entertaining and other entertaining facilities will enable the tourists to be creative while spending their vacation. The third plan of tourist product shall contain its own establishment starting from collection of its own elements up to distribution and usage by tourists. In this stage a main role will be played by management and leadership covering all stages of this tourist product up to the creation of its own brand, which will be known and present within the offer of the operators throughout the world. The forth plan constitutes the creation of tourist product that mainly depends from the policies and the government as a player involved in its creation. In order to provide a shape to a tourist product it is necessary to achieve a full coordination amongst the monetary policies, tourist organization, visa regime, agreements for tourist movements from one place to another, etc. Indeed, this is the most sensitive and complex area when creating a tourist product in Kosovo. As far as the quality part is concerned, in Kosovo this needs to be in compliance with the European level approved standards, such as ISO9000, ISO14000, ISO14002, etc. In terms of adjustment of quality this needs to be done by referring to international quality standards that are determined under the WTO, UNEP, European Commission, for certain types of tourism, gastronomical standards, laws and regulations adopted in Kosovo. Kosovo tourist product quality needs to be a product which the user respectively the tourist demands and is ready to pay for it.

### **3. Kosovo tourist product**

Kosovo has an area of 10,908 km<sup>2</sup> and over 2,000,000 inhabitants. It lies in the center of Western Balkans, and is crossed by important roads linking this part of the Balkan Peninsula in Western Europe and Eastern Europe [Government & KOTAS & GTZ 2008].

Looking from the tourism aspect, Kosovo is divided into five tourism regions:

- Central region of Prishtina;
- Tourist region of Albanian Alps (Cursed Mountains);
- Sharr-tourist region;
- Anamorava-tourist region;

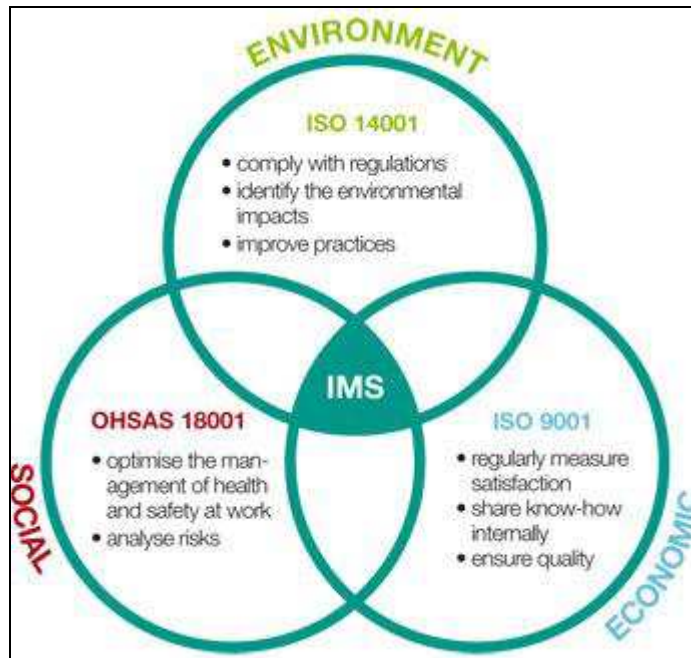
- Mitrovica Tourist region & Shale of Bajgora.

Depending from the constituting elements, the characteristics of Kosovo tourist product can be divided in several groups:

- the future development of Kosovo tourist product will be associated with the enhancement of quality level of local values, (experience, tradition, and heritage).

- Kosovo tourist product is a composition of mainly physical, economical, social, political and ecological elements; therefore it is a multifactor and completed product.

- this tourist product it increasingly based upon scientific-technical achievements, and will adopt the new technologies to provide satisfaction to tourists, which derives as a result of Kosovo local values on which this tourist product was earlier established.



**Figure 2.** An illustration of the sustainable development, according to company “Schmidt.”

Kosovo tourist product must contain parts of the products of the regions and localities, in order to make the development of tourist industry to be in service of national objectives for economic growth, whereby to become a part of the national economical system. Creation of the tourist product is a blend of quantity, quality and continuity of the tourist offer throughout the country. Therefore this tourist product focuses on the improvement of structures of the existing destinations, or in other words known as old destinations, adopting new standards for each offer element by aiming to create a distinctive mark in all levels it is exposed. Other trends in global market make Kosovo tourism to be focus on the formation of the so-called sustainable development which defines the demand to create a sustainable tourist product, in economical, social and ecological aspect, in order to prevent and avoid degeneration of tourist destinations, by providing a new quality to the tourist offer. Sustainable economic development of a country can be achieved in cooperation with the governmental institutions and economic entities. This cooperation needs to be based in its three components, economy, ecology and country's society. These three dimensions of sustainable development have a continuous and mutual interaction by supplementing each other. (Ebner, and Baumgartner 2006). The company cited “Schmidt” has adopted in its business and determined the



sustainable development as one of the ways to contribute in environment protection. Quality, environmental preservation and safety at work contribute to the 3 pillars of sustainable development [Schmidt 2009]. Each is dependent on the other 2 to ensure the equilibrium of the whole structure. Therefore we talk of an Integrated Management System (IMS). The sustainable tourist product not only includes physical components of the tourist destinations which are also protected areas, but the entirety of cultural-historical values and natural beauty of those destinations. In order to determine the quality of sustainable tourism product in the country level, the identification and logging of all parts must be done based on their own value.(Ukaj 2010) Afterwards this tourist product can be defined whether it will satisfy the quantity and quality part of the user-tourist, which is an objective of each enterprise.

#### 4. Conclusion

In order to rapidly develop the tourist offer of the regions and Kosovo as a whole, the development concept has to be viewed in both micro and macro aspects. In micro level it is necessary to:

- appropriately identify and plan the development of micro tourist locations throughout the regions,

In macro level it is necessary to:

- draft, identify and plan the correlation of tourist micro locations in regional tourist destinations and in country level,

- identify and plan supporting activities that aim to develop tourism (quality, cleanliness, traffic, legislation, etc.)

- plan and support development of tourist catering capacities and supplementary tourist contents (hotels, motels, canteens, camping, restaurants, bars etc.), which is a precondition for the tourism development.

It is not preferred to be based on positive emotions of spenders-visitors towards the existing offer, in terms of coming up to the saturation of the tourist offer; therefore it is necessary to pay more attention to the long-term quality of services. Necessarily, quality in tourism should be the focus of attention of players involved in Kosovo tourism, making continuous efforts to update or build more innovative ways of providing services in tourism.

From this it results that:

- Quality needs to be start and end point of each action-activity to be undertaken currently and those to be undertaken in the future,

- it is necessary to make efforts in reaching a better possible quality for products-services that constitute the tourist offer within the tourism-catering market, which is increasingly becoming more selective and refined.

- it is necessary to create and establish a standard within business that will compile "Quality of Regional Values", to standardize the quality of products-services that will facilitate and create the image of Kosovo's Tourist Offer and other related issues.

Creation and implementation of the quality standards is an urgent task, and an invitation to all businesses and institutions. Exchange of experiences from abroad and with countries in the region and wider should work through cooperation in permanent basis which will enable the balance of knowledge and skills, especially with the countries in the region that provide similar tourist offers. Building and developing of tourism offer either in concentrated way or in distributed way from case to case, but its level firstly should be based on fulfilling the conditions of current users of tourism offer and hospitality, but also maximum should be given in order that this offer of geographic regions of Kosovo as a, "tourist destination" can find the right place in: tourist offer of Kosovo, tourist offer of Western Balkan Region, global offer of tourist market



Based on these findings, it appears that it is necessary to conduct an intensive research about the updates and events occurring in tourism markets. This should be a broader activity and managed properly in formation, maintaining and developing tourist products built on the principles of “quality”, based on information collected from interdisciplinary analysis and inter-sector cooperation.

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# THE MODELLING OF THE EVOLUTION OF THE CONCENTRATION OF PESTICIDES ON THE JIU RIVER COURSE

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## Abstract.

*Pesticides are among the most widely used chemicals in the world, and also among the most dangerous to human health. Pesticides can also have chronic health effects both because of acute poisonings and chronic exposure. Many studies have shown adverse health effects on humans. Many of the commonly used household insecticides are organophosphates. These have been linked in many studies to neurological damage in humans. The classic measurements used for pollution evaluation include the biological consumption of oxygen in a 5 days period of time and the chemical oxygen consumption, the amount of oxygen extracted from water by bacteria when agents of pollution are decomposing. The more organic matter can be found in discharged effluents the more the amount of oxygen necessary for decomposition of such pollutants increases and, consequently, the higher the pollution.*

*In this paper, a mathematical model of the evolution of concentrations of pesticides is widely studied. This model is a dynamic bi-dimensional system with three parameters. The variables of the system are the concentration of pollutant and the level of oxygen from water. We achieve this thing by determining both the time trajectories and the evolution of the degrees of oxygenating the waters as a function of the quantity of pollutant for various values of the parameters.*

**Keywords:** pesticides, environment, dynamic bi-dimensional system, GC-MS.

## 1. Sustainable agriculture.

Environmental health, economic profitability, and equity are the goals of sustainable agriculture. The following concepts are integral to sustainable agriculture: understanding of the interrelationship between air, water, and soil; the need to provide farmer and consumer safety; and the commitment to a stewardship of the land. The movement for sustainable agriculture addresses many social and environmental concerns, in addition to promoting innovative and economically viable farming methods such as crop diversification and biological pest control. Sustainable agriculture brings together such aspects of agricultural science as pest management, soil and water conservation, food safety, and animal welfare (Pretty 1995).

Agriculture is a major user of land and water resources and has significant environmental impacts. The main category of pollutants that are found in water and that originate from agricultural activities is nutrients, particularly nitrates, phosphates, various pesticides, farm manure and food processing waste. Agriculture, essentially, is a large and widespread source of pollution.

## 2. The pollution of the Jiu River with pesticides.

Agriculture is an extensive industry using almost 58% of land surface in Jiu River Basin. Agriculture has long been a major source of income for many people living in the Jiu River Basin. But today agriculture is also a major source of pollutants including fertilizers and pesticides, as well as effluent from huge pig farms and agro-industrial units.

Inappropriate agricultural practices in some areas have polluted rivers and groundwater, and led to soil erosion [Candea, and Bran 2001]. Many wetlands have been converted into farmland, drained, contaminated or otherwise degraded. Fertile topsoil has also been eroded in many agricultural regions. These changes have affected the structure and biodiversity of ecosystems.

Unsustainable agricultural practices also reduce the standard of living for farmers and rural communities in the long term.

Jiu River is south of Petrosani, south-western Romania, with the joining of two headstreams rising in the Vulcan and Parang mountains. It then flows south, cutting a wild, deep gorge, the Surduc Pass in the Transylvanian Alps (Southern Carpathians), before flowing into the Danube Plain and into the Danube River in Zaval point. The length of the Jiu River is about 205 miles (339 km). The most important tributaries of the Jiu River are: Motru, Gilort, Amaradia, and the biggest cities are: Petrosani, Tg. Jiu, Filiasi, and Craiova.

The significant point source pollutions with pesticides from Jiu hydrographical river basin are: industrial: Doljchim Craiova and agricultural: farms pollution by products used in agriculture such as fertilizers or pest killers (nitrogen compounds –  $\text{NH}_4$ ,  $\text{NO}_2$  and  $\text{NO}_3$ , phosphates, pesticides etc), either on the areas where such producers are located (DOLJCHIM Craiova) or in the fields, due to inadequate use. Such diffuse pollution mainly damaged the individual wells in the rural areas, but also groundwater catchments.

The Jiu corridor presents many pollution sources like chemical factories producing caustic soda, pesticides and fertilizers. One of the most polluted zones is the DOLJCHIM Craiova industrial area. Polluted waters coming from chemical industry are retained in many ha storage basins located in the vicinity of the DOLJCHIM Craiova reservoir. These basins, delineated by permeable earth dikes, are the source of the pollutants infiltrated in the aquifer; small thickness layers of fine clay and sandy clay form the unsaturated soil.

Water and groundwater contamination, resulting from the use of various pesticides, is becoming a growing concern. Pesticides generally have low solubility in water and are usually manufactured in powder form, as suspension concentrates or as miscible liquids (Hayes 2004). The occurrence of pesticides in groundwater is widely recorded in all the rivers basins of our country. The most widely reported pesticide is the herbicide atrazine. Atrazine is one of the few herbicides that may pose a potential health risk to mammals and in some countries (e.g. Germany, Austria) its use is already prohibited. Agrochemicals are usually diluted with water and then they are sprayed over soil or over growing crops. More problematic is the disposal of unused spray material and the contaminated water, which is produced when spraying equipment, is washed out. This unfortunately happens near or sometimes directly in natural waters especially if they are found in the near vicinity. Since pesticides are designed to kill, it is no surprise that in the aquatic environment they destroy flora and fauna and threaten the human population by contaminating sources of drinking water.

Pesticides are persistent and non- biodegradable and they can be bioaccumulate through the biologic chains: soil-plant-food and seawater-marine organism-food (Shawi, and Dahl 1999). The presence of some pesticides may persist in soils for long periods of time and repeated use can lead to its accumulation in the ground. This could lead to crop toxicity and a decline in soil organisms (Pimental 1995).

To determine the content of pesticides in the samples of water taken from several points of the Jiu River, an analytical method has been used: gas chromatography with mass spectrometry detection.

### 3. Mathematic Models.

The economic models dated after 1950 mainly referred to the production dynamics. The following stage consisted of the improvement of the previous models, by including social criteria, such as those connected to welfare, poverty, etc. After 1980, restrictions have been introduced regarding the environment. This new evolution occurred as a consequence of an increasing concern for the environment as a main factor determining the quality of life.

Various types of pollution (water pollution, traffic pollution, noise effects, soil pollution, etc.) may be simulated mathematically, using new approaches, different from the classic ones. For this purpose, the dynamic systems prove to be very useful. The study of those systems provides the possibility to signal the interactions between the specific parameters, being a flexible method of optimally determining those parameters.

Dynamic systems, studying determinist processes, have known an extraordinary development in the past years, as applications in various domains such as physics, chemistry, engineering, and ecology. A process is considered to be determinist if its subsequent and past behaviour is uniquely determined by its present state; the dynamic system is the mathematical model of a determinist process.

The usage of the dynamic model may outline through objective indicators the main characteristics and evolutions of the quality of water; with its help, one may register many dysfunctions with the most serious consequences on the environment. Through it, the environment policies become mostly anticipative.

The mathematical modelling is some from most important instrument of scientific cognition; with its help we can realize a conventional image objects research, a simplification representation of reality. The model is a facsimile with degree of variable difficulty of real world or a parts component of them. The understanding of this phenomena segments of reality tackles, know in detail, quotient and act about phenomena analyses motivate the reason appealed to such representations. Most dense used-up idiom is the mathematical idiom. Afterwards, we appealed at this for surprised with a dynamic model the complex behaviour for a system, for emphasize how structure variables determine the trajectories, respectively the temporally behaviour.

#### 4. Experimental

The samples have been taken in three months: January 2008, April 2008, July 2008, and October 2008. These represent four seasons: winter, spring, summer and autumn. Were determined some of the most dangerous pesticides from Jiu River, from seven different points of the Jiu River. These points were: (1) Campu' lui Neag (The West Jiu); (2) Livezeni (The East Jiu); (3) upstream the confluence with Sadu; (4) Balteni; (5) Podari; (6) Malu Mare and (7) Zaval, the point where the Jiu River flows into the Danube.

Samples must be collected in glass containers. The distance from the river side is about 2.00 – 2.50 meters and the depth was about 0.20 – 0.50 meters (Stoica, Stanescu, and Baiulescu 2003). Conventional sampling practices should be followed; however, the bottle must not be prerinced with sample before collection. The samples must be iced or refrigerated at 4°C away from light from the time of collection until extraction. Preservation study results indicated that most method analytes present in samples were stable for 14 days when stored under these conditions (Suess 1982).

The GC-MS is composed of two major building blocks: the gas chromatograph and the mass spectrometer. The gas chromatograph utilizes a capillary column which depends on the column's dimensions (length, diameter, film thickness) as well as the phase properties (e.g. 5% phenyl polysiloxane). The difference in the chemical properties between different molecules in a mixture will separate the molecules as the sample travels the length of the column. The molecules take different amounts of time (called the retention time) to come out of (elute from) the gas chromatograph, and this allows the mass spectrometer downstream to capture, ionize, accelerate, deflect, and detect the ionized molecules separately [McMaster, and McMaster 1998]. The mass spectrometer does this by breaking each molecule into ionized fragments and detecting these fragments using their mass to charge ratio. These two components, used together, allow a much finer degree of substance identification than either unit used separately.

#### 4.1. Mathematical model

The pesticides enter in the water at a constant rate. Bacterial action metabolizes (decomposes) the pollutant at a rate proportional to its mass. In doing so, the dissolved oxygen in the water is used up at the same rate that the pollutant decomposes. However, oxygen in the air re-enters the lake through surface-to-air contact (this is called re-aeration) at a rate proportional to the difference between the maximum dissolved oxygen level that the lake can support and its current actual value.

To find the dissolved oxygen level  $x$ , in the water at any time, observe that its rate of change depends on an input that is proportional  $y$  and with the deficit of oxygen  $x_m - x$ , where  $x_m$  is the maximum (saturation) level of oxygen in respective water, and an output that is proportional to the mass  $y$  of the pesticides. Is obtained thus first equation for represents the evolution of this level, temporally, depending on the mass of pollutant (Beltrami 1990):

$$\dot{x} = \beta(x_m - x) - \alpha y$$

where  $\alpha$  and  $\beta$  are constants. At the same time, the rate of change  $y$  depends on the constant input rate  $\sigma > 0$ , and a decay rate is linear in  $y$  itself. Thus, we can write:

$$\dot{y} = \sigma - \alpha y$$

Obtain thus, a dynamic linear affine system, bi-dimensional, which depends on three real parameters ( $\alpha$ ,  $\beta$  and  $\sigma$ ) by means of whom we can cause as much evolution temporally degrees of they oxygenate the waters and amount of pollutant gift and dependent degrees of pollute the waters depending on mass of pollutant. In the above-mentioned conditions evolution amount of oxygen in water is governed of problem Cauchy  $x(0) = x_0$ ,  $y(0) = y_0$  for the system of differential equation of the first order:

$$\begin{cases} \dot{x} = -\beta x - \alpha y + \beta x_m \\ \dot{y} = -\alpha y + \sigma \end{cases}$$

Because it is a dynamic linear afin system the discrepancy among it and liniarized is translation equilibrium to origin. The two systems are topologic equivalent, indifferently of the type equilibrium (Arrowsmith, Place 1990).

#### 5. Results and discussions

In the Table No.1 are presented the highest concentration admitted by Romanian standard for different pesticides [order no.1146, 2002].

**Table 1.** The highest concentrations admitted by Romanian standard

s	Pesticide	Measure Units	Concentrations values – Romanian standard		
			I	II	III
<b>a. Organochlorine pesticides</b>					
	DDT	mg/L	0,1	0,1	0,5
	Lindane	mg/L	0,01	0,1	0,5
<b>b. Organophosphorus pesticides</b>					
	Diazinon	mg/L	0,03	0,03	0,1
<b>c. Carbamates pesticides</b>					
	Atrazine	mg/L	0,01	0,1	0,5

The quality classes are:

I - very good; II - moderate; III - week.

**DDT** is moderately toxic, with a rat  $LD_{50}$  of 113 mg/kg [The WHO Recommended Classification of Pesticides by Hazard, 2005]. The highest concentration of DDT admitted is 0, 1 mg/L. Organochlorine compounds in general and DDT specifically has been linked to diabetes (Codru 2007).

**Lindane.** The highest concentration of Lindane admitted is 0,1 mg/L.

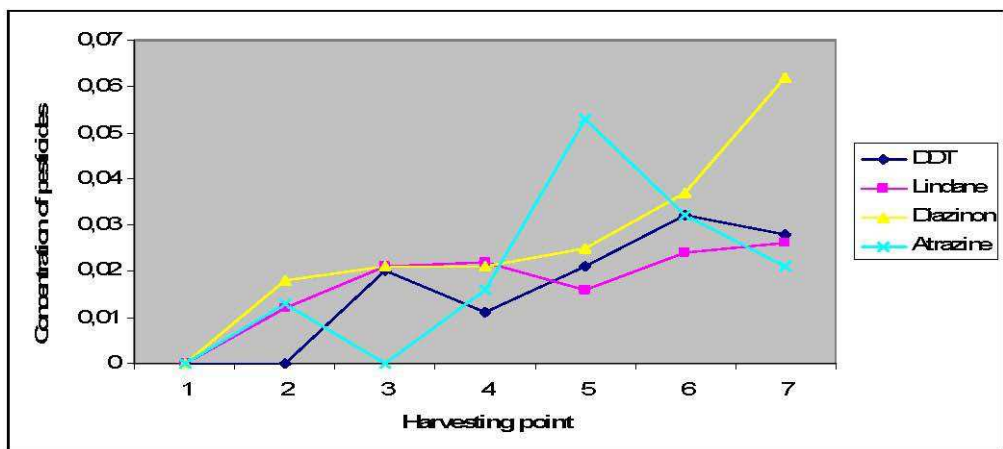
The EPA and WHO both classify lindane as "moderately" acutely toxic (The WHO Recommended Classification of Pesticides by Hazard, 2005). Most of the adverse human health effects reported for lindane have been related to agricultural uses and chronic, occupational exposure of seed treatment workers (Dacre, and Jennings 1970).

Lindane is a persistent organic pollutant: it is relatively long-lived in the environment, it is transported long distances by natural processes like global distillation, and it cans bioaccumulate in food chains (Kolpin, Furlong, and Meyer 2002).

**Diazinon** is a thiophosphoric acid ester. The highest concentration of Diazinon admitted is 0, 03 mg/L. Diazinon is classified as slightly toxic to moderately toxic [The WHO Recommended Classification of Pesticides by Hazard, 2005]. Death has occurred in some instances from both dermal and oral exposures at very high levels (Vettorazzi 1976).

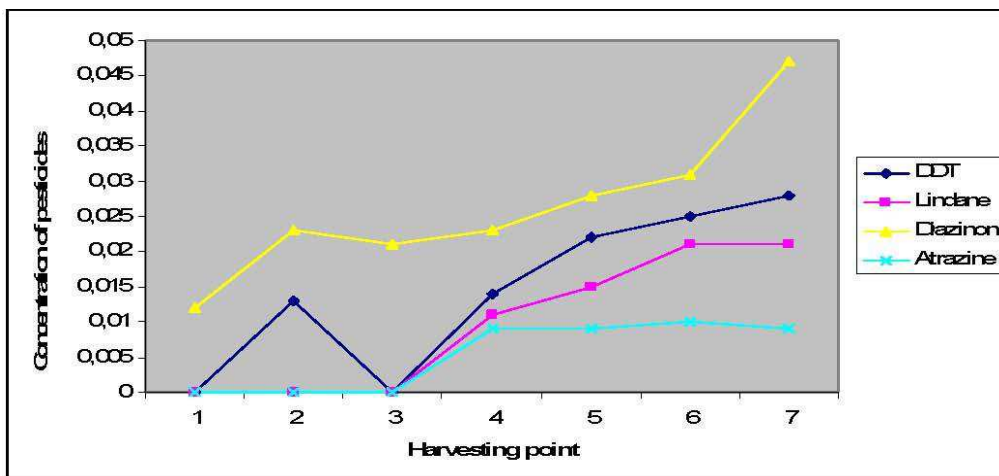
**Atrazine** was banned in the European Union (EU) in 2004 because of its persistent groundwater contamination (Ackerman 2007). The highest concentration of Atrazine admitted is 0, 1 mg/L.

Fig. 1 shows the variation of the concentration of some pesticides in the samples taken from the Jiu River in January 2008. The concentration for Lindane in all the harvesting points does not overtake the admitted limit. The concentration of Diazinon grows relatively constant from Campu' lui Neag to Zaval, but in Malu Mare and Zaval points the Diazinon concentration overtakes the admitted limit.



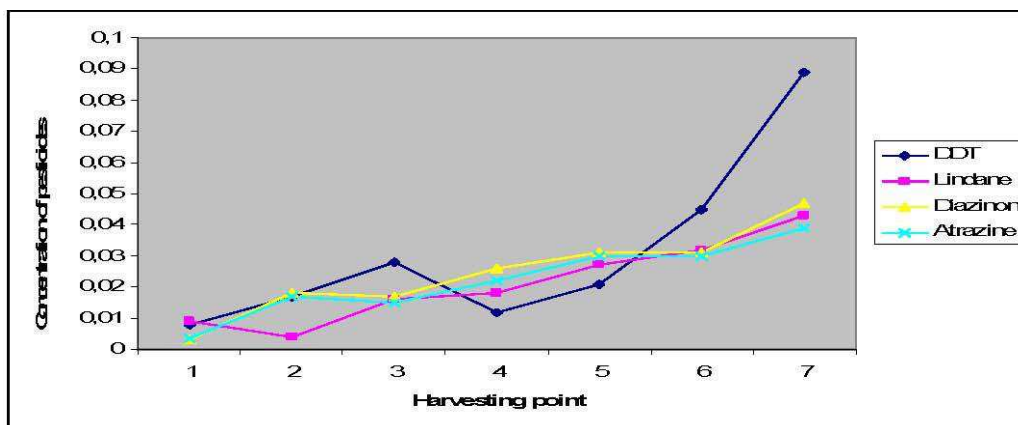
**Figure 1.** The concentration of some pesticides (mg/L) in the samples taken from the Jiu River in January 2008

Fig. 2 shows the variation of the concentration of some pesticides in the samples taken from the Jiu River in April 2008. Of all analyzed pesticides, the Diazinon concentration overtakes the admitted limit in Malu Mare and Zaval points.



**Figure 2.** The concentration of some pesticides (mg/L) in the samples taken from the Jiu River in April 2008

Figure 3 shows the variation of the concentration of some pesticides in the samples taken from the Jiu River in July 2008. The concentration of DDT grows in Zaval point, but doesn't overtake the admitted limit. The concentration of Diazinon grows after Balteni point, and overtakes the admitted limit after this point.

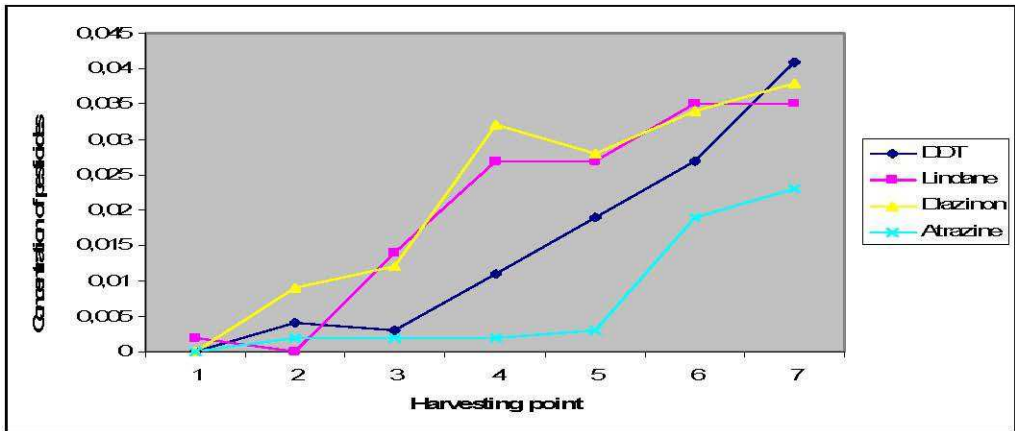


**Figure 3.** The concentration of some pesticides (mg/L) in the samples taken from the Jiu River in July 2008

Fig.4 shows the variation of the concentration of some pesticides in the samples taken from the Jiu River in October 2008. The concentrations of DDT, Lindane and Atrazine grow constantly from (1) point Campu' lui Neag to (7) point Zaval, but don't overtake the admitted limit.

The concentration of Diazinon grows after Balteni point, and overtakes the admitted limit after this point. In the Table no. 2 are presented the levels of dissolved oxygen during the four seasons we made the study in.





**Figure 4.** The concentration of some pesticides (mg/L) in the samples taken from the Jiu River in October 2008

**Table 2.** The levels of dissolved oxygen during the four seasons

o.	The season	Measure units	Dissolved Oxygen
.	Winter	mg/L	9,13
.	Spring	mg/L	10,96
.	Summer	mg/L	12,71
.	Autumn	mg/L	12,34

### 5.1. Equilibrium and phase portrait

The points of equilibrium to this system are the solutions  $\bar{u} = (x, y)$  of the algebraic systems:

$$\begin{cases} -\beta x - \alpha y + \beta x_m = 0 \\ -\alpha y + \sigma = 0 \end{cases}$$

The system admits the unique solution  $\bar{u} = (x_m - \frac{\sigma}{\beta}, \frac{\sigma}{\alpha})$ . The linearized of the system

around this point is:

$$\begin{cases} \dot{X} = -\beta X - \alpha Y \\ \dot{Y} = -\alpha Y \end{cases}$$

With associated matrix  $A = \begin{pmatrix} -\beta & -\alpha \\ 0 & -\alpha \end{pmatrix}$ . We study (Ungureanu 2009)  $\bar{u}$  is hyperbolic, but

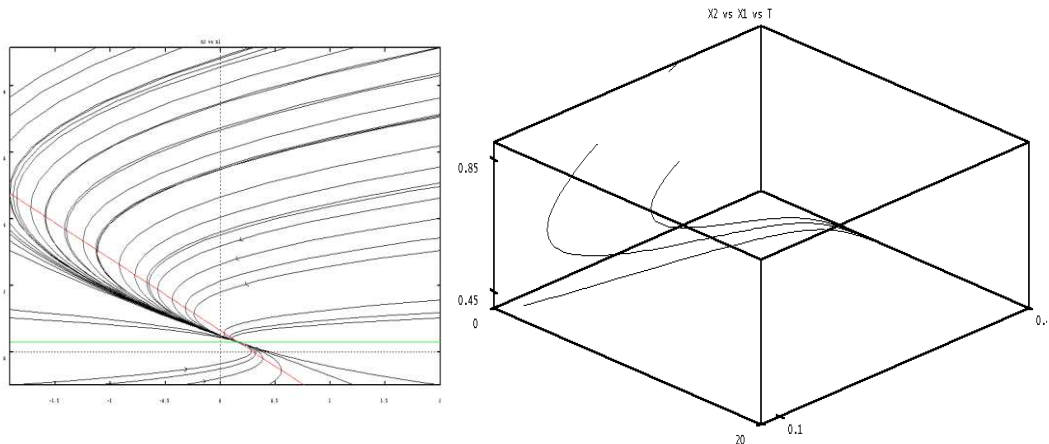
if  $\text{Re } \lambda_1 = 0$  or /and  $\text{Re } \lambda_2 = 0$  we say as the equilibrium is nonhyperbolic.

Characteristic equation is  $\lambda^2 + (\alpha + \beta)\lambda + \alpha\beta = 0$ , with  $\Delta = (\alpha - \beta)^2$ .

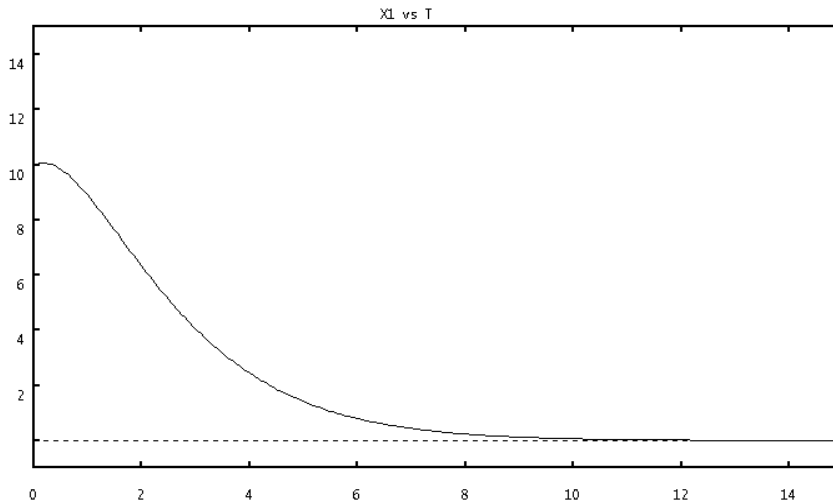
We can comment on the behaviour systems thus:

1. If  $\alpha > 0$  and  $\beta > 0$  (one from the situations most frequently meet) the eigen values are negative, therefore the system is stable,  $\bar{u} = (x, y)$ , node attractive, situation in which trajectories tending to the point of equilibrium (fig. 5, a). If  $\alpha = \beta$  the equilibrium becomes the attractive node after infinity of asymptotic direction, the eigenvector be in this situation  $\bar{v} = (a, 0)$ ,  $a \in R$ .

Departing from the idea as the any model is banked on yes and real former appealed to wage the shoppo review for the graphic representation (fig.5, b). Thus, we find as  $x$  can take, depending on the quality impure waters (gray or black) the values between 0. 1 and 0. 5. The level of saturation of oxygen is  $x_m = 0.7 (g / m^2 \times h)$ . Let the initial values  $x_0 = 0.3$ ,  $y_0 = 0.011285$ , and for parameters  $\alpha = 2$ ,  $\beta = 4.3$ ,  $\sigma = 0.6$ . We obtain the point of equilibrium of coordinately  $\bar{u} = (x, y) = (0.6, 0.0465116)$ .



**Figure 5.** The compoment of the system for  $\alpha > 0, \beta > 0$   
a) The attractive node; b) The trajectories in  $(x,y,t)$ - space



**Figure 6.** Trajectories for the model in cas



In this way we obtained and theoretical, noticed from Figure 6 the trajectories tending, temporally, to the point of stable equilibrium.

1. If  $\alpha\beta < 0$  the system is unstable, and the point of equilibrium is saddle point. In this case the directions invariance are the directions of vectors,  $\bar{v}_1 = (1, \frac{\alpha - \beta}{\alpha})$ , respectively  $\bar{v}_2 = (1, 0)$ . Here the behaviour systems depends great deal of the initial conditions.

2. In unusual situation  $\alpha < 0$  and  $\beta < 0$  the system is strong unstable, and the point of equilibrium is the repulsive node.

## 6. Conclusions

Concerning the containing of pesticides of the Jiu River, in 2008, the water of the Jiu River are from I class of quality, from (1) Campu' lui Neag point to (4) Balteni, and from II class of quality from (4) Balteni to (7) Zaval, the meeting point with Danube River.

The containing of pesticide of the Jiu River course is bigger in summer and autumn than winter and spring.

The modelling of this phenomenon can let us causes a value of equilibrium and his gives estimates it a temporally behaviours of them. This dynamics is reflecting the diminishing of the punctiform emissions, mainly in industry and agriculture, as a direct result of cutting down the economic activity but also as a result of applying more extensive steps of protection as far as the water quality is concerned, as comparatively with the previous period, before 1989. As far as the phreatic waters are concerned, there are certain areas within the rural space, where relatively high concentrations of nitrogen and pesticides (DTT and Diazinon), still persist.

However, to provide models for environmental systems is a difficult matter, owing to the complexity of the systems and of interactions that they have had with various other systems, an interaction which is sometimes difficult to determine.

For the future, we intend to develop a more complex model, taking into account the interaction between the physical and chemical factors (temperature, salinity, light, nutrients, water agitation) and the biological ones (the presence of an algae population in the area).

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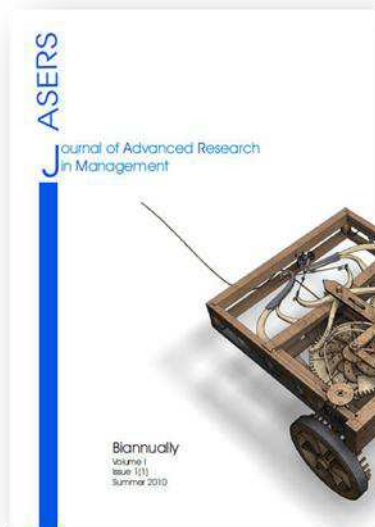
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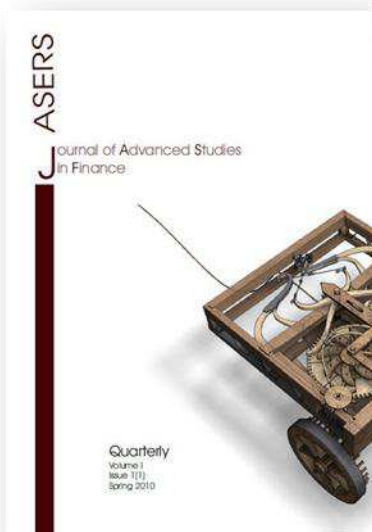
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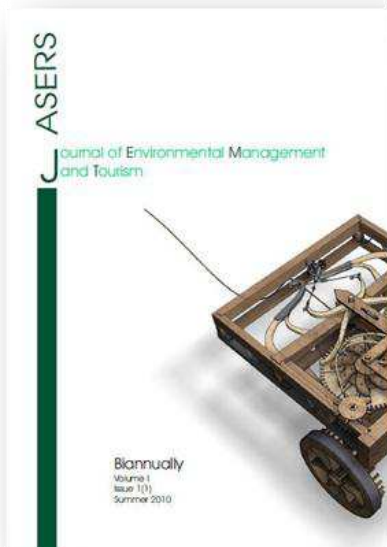
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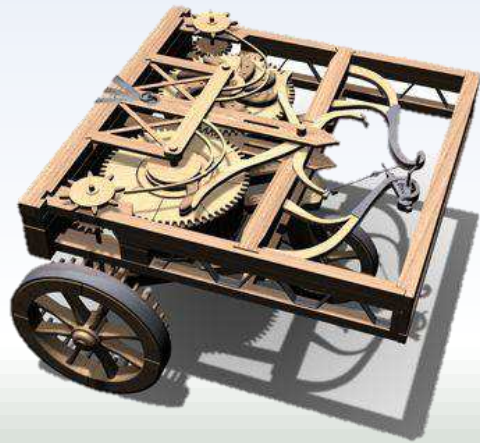
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