

TABLE 1. Repeatability and the Effect of Scanning Time on FPXRF Results

Sample [†]	Time, sec	Mean, %	SE	S.D.	Sample Variance	Kurtosis	Skewness	Range	Confidence Level (95%)
Low Ca	30	4.48	0.07	0.21	0.04	-1.01	0.33	0.62	0.15
	60	4.47	0.06	0.18	0.03	-0.73	0.76	0.54	0.13
	90	4.60	0.06	0.19	0.04	-0.54	0.24	0.60	0.14
Medium Ca	30	13.90	0.20	0.63	0.39	-1.06	-0.37	0.93	0.45
	60	14.04	0.10	0.32	0.10	-0.77	-0.71	0.97	0.23
	90	14.03	0.12	0.39	0.15	3.30	1.66	1.35	0.28
High Ca	30	16.01	0.18	0.57	0.33	3.26	-1.49	2.05	0.41
	60	15.64	0.13	0.42	0.18	5.70	2.22	1.45	0.30
	90	15.65	0.12	0.39	0.15	-0.86	-0.10	1.23	0.28

[†]Low (>5%), medium (5%–15%), and high (>15%).

MATERIALS AND METHODS

An Innov-X Systems Alpha series FPXRF (Innov-X Systems, Inc, Woburn, MA) with tantalum X-ray tube operated at 35 kV was used in this study. Its field-oriented design enables *in situ* determination of soil total Ca with no need of any preparation processes. Ten artificial soil samples were constructed by carefully weighing (± 0.0001 g) and mixing reagent-grade gypsum powder and washed quartz sand (<2mm) in different quotients for scanning with FPXRF. Seventeen soil samples with varying levels of Ca were collected in the field from six sites in West Texas and eastern New Mexico. These 17 samples were first scanned with FPXRF, then total Ca content was determined by ICP-AES using total digestion with nitric and sulfuric acid (Soil Survey Staff, 2004), and lastly, calcite and gypsum percentage were quantified using X-ray diffractometry (XRD) (Eberl, 2003). It should be noted that soil digest analyzed by ICP-AES is considered the standard method for total Ca determination. For quantitative X-ray diffraction analysis, samples were scanned on a Siemens D5000 X-ray diffractometer (40 kV, 30 ma) at 0.02° 2θ steps, 2 sec per step, from 2 to 70° 2θ . Zincite (ZnO) was used as an internal standard. Quantitative interpretations of XRD data were made with RockJock software (Eberl, 2003). An additional 31 anonymous ground soil samples with variable levels of total Ca were obtained from Texas A&M

University's Soil Characterization Database and scanned with FPXRF. Calcite percentage was determined using the gasometric procedure of Dreimanis (1962). Gypsum percentage was determined by precipitation with acetone (U.S. Salinity Laboratory Staff, 1969).

Factors Influencing FPXRF Readings

The 17 field samples collected for this study were scanned in triplicate for 60 sec each. To examine the factors influencing FPXRF readings, FPXRF scanning was conducted under five different conditions for each sample: in the field (F), through the bags of moist samples (B), through the bags of oven-dried samples (B&D), through the bag of dried, ground, and sieved samples (B&D&G), and directly on the surface of dried, ground, and sieved samples (D&G). The sample bags used were standard Ziploc freezer bags.

RESULTS

Repeatability of the FPXRF and the Effect of Scanning Time Length

To cover the wide measurement range of FPXRF, three air-dried natural soil samples with low (>5%), medium (5%–15%), and high (>15%) total Ca content were selected. With the

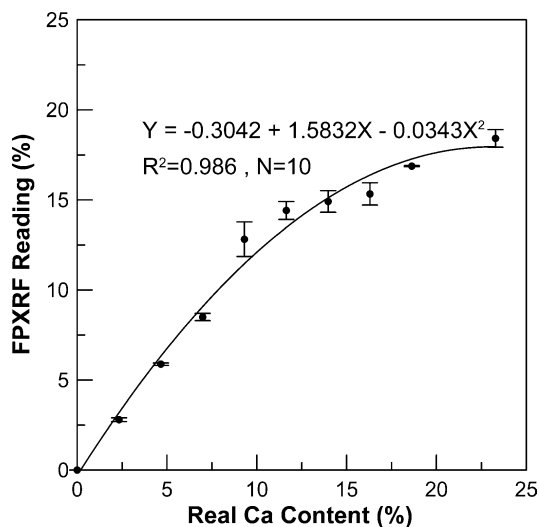


FIG. 1. The FPXRF readings versus true Ca contents of artificially constructed samples.

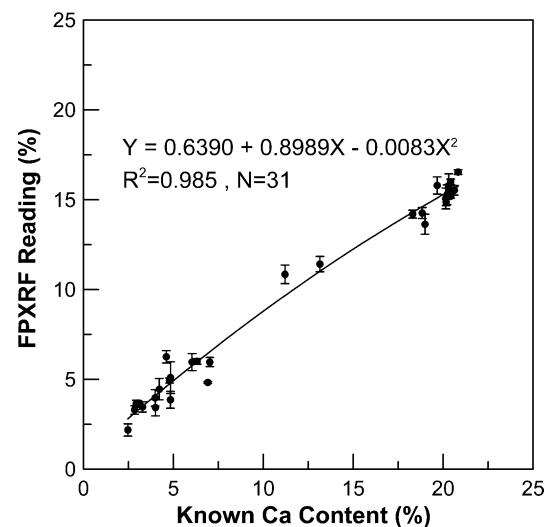


FIG. 2. The FPXRF readings versus known Ca contents of TAMU soil characterization samples.

TABLE 2. The ICP, XRD, and FPXRF Measurements of Soil Ca Content

Site	Depth, cm	ICP		XRD	F [†]		B [‡]		B, D [§]		B, D, G		D and G	
		Mean, %	S.D.		Mean, %	S.D.	Mean, %	S.D.	Mean, %	S.D.	Mean, %	S.D.	Mean, %	S.D.
1	0–4	6.34	0.11	10.41	7.14	0.16	5.77	0.01	6.20	0.38	6.08	0.09	7.16	0.32
	4–10	19.53	0.31	22.10	15.34	0.39	14.45	0.17	15.52	0.40	15.25	0.46	16.43	0.02
	10–30	20.50	0.77	23.23	17.49	0.88	15.80	0.38	16.59	0.45	16.24	0.79	17.94	0.58
2	0–6	3.70	0.03	15.50	4.59	0.47	4.19	0.26	4.39	0.24	4.20	0.20	4.50	0.17
	6–20	5.66	0.00	19.76	4.98	0.53	5.46	0.70	4.91	0.25	4.94	0.11	5.80	0.22
	20–30+	4.90	0.36	18.63	4.47	0.49	4.53	0.04	4.40	0.46	5.02	0.32	5.08	0.29
3	18–36	2.84	0.05	16.25	4.69	0.86	4.06	0.57	3.54	0.59	3.51	0.20	4.49	0.28
	53–81	4.97	0.47	10.66	7.49	0.63	6.91	1.62	5.95	0.42	5.78	0.19	7.65	0.83
	81–130	6.47	0.25	15.76	8.11	0.82	10.47	0.43	8.80	1.76	7.16	1.21	8.16	0.66
4	130–150	4.57	0.29	10.58	6.07	1.45	5.62	0.59	4.46	0.26	4.75	0.24	5.78	0.21
	3–20	20.10	0.87	22.85	17.84	0.41	15.51	0.24	16.58	1.14	15.28	0.50	18.16	0.60
	58–89	17.38	0.13	21.53	15.69	0.91	15.02	1.40	13.27	0.25	14.35	0.41	16.90	0.31
5	157–176	4.13	0.11	6.51	5.37	0.25	4.90	0.81	3.79	1.01	5.62	0.27	5.49	0.65
	25–48	13.42	0.58	21.81	13.75	0.85	11.90	0.31	12.70	0.20	10.83	0.21	13.62	0.08
	71–102	13.00	0.20	23.05	14.28	0.46	12.51	0.22	12.82	0.58	12.41	0.41	14.71	0.45
6	102–160	13.01	0.57	22.38	13.90	1.46	10.94	1.26	13.04	0.99	10.91	0.04	13.94	0.23
		20.17	0.72	23.04	18.49	0.24	15.95	0.66	15.80	0.40	16.00	0.34	17.90	0.33

[†]Field, [‡]bagged, [§]dried, ^{||}ground.

FPXRF directly contacting the sample surface, each sample was measured 10 times with scanning time lengths of 30, 60, and 90 sec. Results indicate that at all levels of Ca (low, medium, and high), the repeatability of the FPXRF is acceptable in terms of SE, S.D., variances, and confidence levels (Table 1). The readings of FPXRF become more stable as the scanning time increases, as evidenced by decreases in SE, S.D., and confidence level. However, *t* tests applied to the readings of different scanning times, as well as to the means of each data set, indicate that they are not significantly different. Considering both scanning time and value stability, 60 sec provides optimal results for practical application.

T1

Accuracy of FPXRF in Ca Determination

Samples Derived from Mixed Reagents

Within the 10 artificially constructed soil samples containing 0%, 10%, 20%, 30%, 40%, 50%, 60%, 70%, 80%, and 100% gypsum, the Ca percentages of these samples were 0%, 2.33%, 4.66%, 6.98%, 9.31%, 11.64%, 13.97%, 16.30%, 18.63%, and 23.28%, respectively. Three FPXRF readings were taken on each sample surface. Figure 1 indicates that

F1

FPXRF readings are closely correlated with true Ca concentrations of the samples ($R^2 = 0.986$, $n = 10$), and their relationship can be described by a second-order polynomial equation.

Soil Characterization Samples

The 31 dried and sieved (<2mm) samples from the Texas A&M University soil characterization laboratory were scanned with FPXRF in triplicate for 60 sec each. Concentrations of elemental Ca in these samples were calculated from calcite and gypsum percentages available in the Texas A&M University Soil Characterization Database. Similar to the artificially constructed soil samples, a second-order polynomial equation fits the relationship between Ca concentrations and FPXRF readings quite well ($R^2 = 0.985$; Fig. 2).

F2

The ICP results are highly correlated with FPXRF readings from all five treatments, whereas XRD was prone to overestimate soil Ca contents, particularly at low Ca levels (Tables 2 and 3). In addition, FPXRF readings are highly correlated among all five treatments (Table 3). Although the processes of sample drying, grinding, and sieving somewhat affect the FPXRF readings, soil total Ca contents still can be satisfactorily obtained based on

T2T3**TABLE 3.** Coefficients of Determination Between Sample Treatments

	ICP	XRD	F [†]	B [‡]	BD [§]	BGD	GD
ICP	1						
XRD	0.774	1					
F	0.977**	0.750*	1				
B	0.966**	0.747*	0.978**	1			
BD	0.978**	0.791*	0.987**	0.980**	1		
BGD	0.992**	0.758*	0.984**	0.979**	0.980**	1	
GD	0.984**	0.765*	0.996**	0.982*	0.988**	0.991**	1

[†]Field, [‡]bagged, [§]dried, ^{||}ground.

AQ2

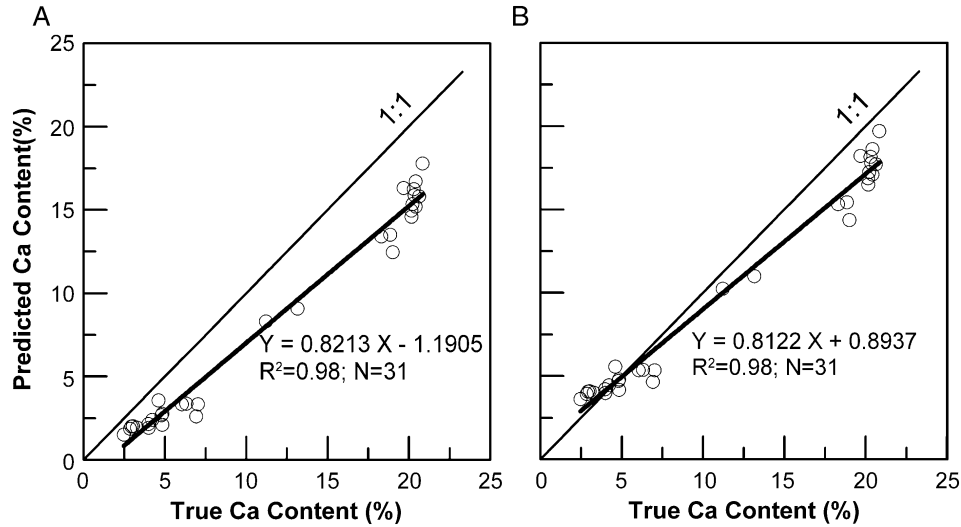


FIG. 3. True Ca contents versus predicted Ca contents of TAMU soil characterization samples using calibration curve (A, derived from the artificially constructed soil; B, derived from the field samples).

FPXRF readings with one of the five treatments if the calibration is conducted using the same treatment. Specifically, sample grinding and sieving decrease the S.D. for most samples, implying that a high degree of heterogeneity of soil Ca exists in the field. Acceptable measurements using FPXRF in the field may require multiple readings to be taken. Scanning directly on the soil sample surface consistently produced higher readings than scanning through the plastic bags. This is likely caused by part of the wave signals from the soil samples being disrupted by the bag itself and/or diffused by the bag surface. The effect can be easily reduced through consistent calibration, suggested by the high coefficients between the through-bag and on-surface readings (Table 3).

DISCUSSION

As previously shown, the repeatability and accuracy of the FPXRF are acceptable. However, it is necessary to check its calibration quality before any practical application. Theoretically, the FPXRF can be further calibrated in the factory using standard materials such as the artificial soils constructed in this study. Furthermore, calibrations can be constructed and applied by analyzing field samples using standard laboratory methods. For example, using the 10 artificially constructed soils, the following calibration curve was obtained (Eq. [1]):

$$Y = 1.2357 - 0.0110X + 0.0612X^2 (R^2 = 0.965, N = 10) \quad (1)$$

in which Y represents predicted total Ca content and X represents FPXRF readings. Using the 17 field samples obtained in this study, the following calibration curve was obtained (Eq. [2]):

$$Y = 3.4327 - 0.0518X + 0.0626X^2 (R^2 = 0.987, N = 17) \quad (2)$$

F3 Using these two curves, Figs. 3 A and B show the predicted soil Ca content of the samples from the Texas A&M University soil characterization laboratory against true Ca contents. Clearly, the soil Ca contents are somewhat underestimated in this case because the slopes are considerably less than one. However, it should be noted that the predicted and true Ca contents are highly correlated in a linear relationship,

which means that the predictions can be easily improved if specific calibration processes have been conducted. It should also be noted that the true Ca contents of the Texas A&M samples were calculated from the calcite and gypsum percentages only. Other Ca-bearing minerals could easily account for the discrepancy observed between FPXRF data and the “true” Ca content considered. Furthermore, the accuracy of laboratory methods for gypsum quantification remains controversial (Nelson Rolong, personal communication, 2008). Thus, the reported soil gypsum content in the Texas A&M University Soil Characterization Database could deviate from the real values. Similarly, the percentage of calcite determined by acidification is actually calculated from the quantity of used acid, which can be affected by all soil carbonates and even some organic materials (Zougagh et al., 2005). The predictions can possibly be improved if standard analytical methods such as ICP-AES are applied to determine

AQ3

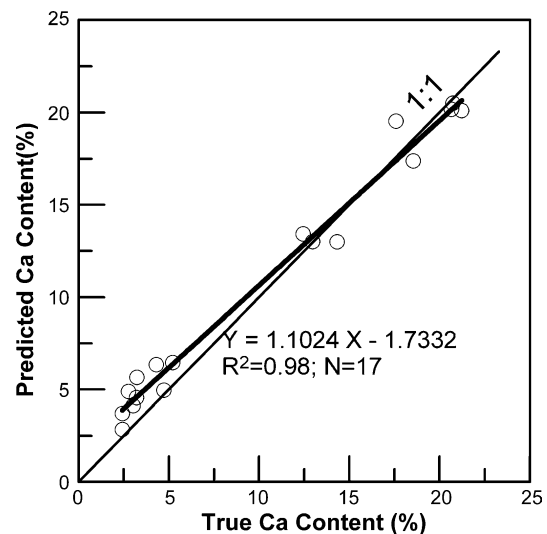


FIG. 4. True Ca content versus predicted Ca content of field soil samples using artificially constructed soil samples.

the true Ca content. Using Eq.(1), we can also predict soil Ca content of the 17 field samples collected in this study (Figs. 1 and 4). Although soil Ca contents are still somewhat underestimated, particularly for the lower range, the predictions are considerably improved because the slope of the fitting line is very close to one.

CONCLUSIONS

As an instrument designed for field work, FPXRF has several advantages in detecting and quantifying soil Ca concentration. Field work and laboratory results show that it is not only fast and convenient (short scanning time and no need of sample collection), but also has high consistency and repeatability (Table 1). As FPXRF readings are closely correlated with true soil Ca contents (Tables 2 and 3), high accuracy can be readily achieved along with additional sample collection and comprehensive calibration.

Sample treatments including drying, grinding, and sieving did not significantly affect the means of soil Ca content. Sample grinding and sieving reduced the S.D. of FPXRF readings (Table 2). Scanning with FPXRF through sample bags substantially but proportionally reduces FPXRF readings. However, this effect can be offset easily via calibration, as evidenced by the close relationship between FPXRF readings of direct contact and bagged samples. More investigations of FPXRF are warranted to account for variability in field conditions (moisture, soil texture, etc).

ACKNOWLEDGMENTS

The authors thank the USDA-NRCS for assistance in field sampling. The authors thank Nelson Rolong, Tom Hallmark, Ray Ferrell, B. L. Allen, Wayne Hudnall, and Juan Hererro for their input, discussion, and guidance in this investigation. The authors also thank the two anonymous reviewers for their invaluable suggestions. Finally, the authors thank Innov-X Systems for a research grant that funded part of this research.

REFERENCES

- Arslan, Z., and J. F. Tyson. 1999. Determination of calcium, magnesium and strontium in soils by flow injection flame atomic absorption spectrometry. *Talanta* 50(5):929–937.
- Beccaglia, A. M., C. A. Rinaldi, and J. C. Ferrero. 2006. Analysis of arsenic and calcium in soil samples by laser ablation mass spectrometry. *Anal. Chem. Acta* 579:11–16.
- Bintz, W. W., and D. J. Butcher. 2007. Characterization of the health of southern Appalachian red spruce (*Piceae rubens*) through determination of calcium, magnesium, and aluminum concentrations in foliage and soil. *Microchem. J.* 87:170–174.
- Cheng, K. L., and R. H. Bray. 1951. Determination of calcium and magnesium in soil and plant material. *Soil Sci.* 72:449–452.
- Cheng, K. L., T. Kurtz, and R. H. Bray. 1952. Determination of calcium, magnesium and iron in limestone. *Anal. Chem.* 24:1640–1643.
- Dreimanis, A. 1962. Quantitative gasometric determination of calcite and dolomite by using the Chittick apparatus. *J. Sediment Petrol.* 32:520–529.
- Eberl, D. D. 2003. User's Guide to Rockjock—A Program for Determining Quantitative Mineralogy From Powder X-ray Diffraction Data. US Geol. Surv., Open File Report 03–78.
- Gómez-Ariza, J. L., D. Sánchez-Rodas, I. Giráldez, and E. Morales. 2000. A comparison between ICP-MS and AFS detection for arsenic speciation in environmental samples. *Talanta* 51(2):257–268.
- Herpin, U., C. C. Cerri, M. C. S. Carvalho, B. Markert, J. Enzweiler, K. Friese, and G. Breulmanne. 2002. Biogeochemical dynamics following land use change from forest to pasture in a humid tropical area (Rondonia, Brazil): A multi-element approach by means of XRF-spectroscopy. *Sci. Total Environ.* 286:97–109.
- Hettipathirana, T. D. 2004. Simultaneous determination of parts-per-million level Cr, As, Cd and Pb, and major elements in low level contaminated soils using borate fusion and energy dispersive X-ray fluorescence spectrometry with polarized. *Spectrochim. Acta, Part B: Atom. Spectrosc.* 59:223–229.
- Kalnicky, D. J., and R. Singhvi. 2001. Field portable XRF analysis of environmental samples. *J. Hazard. Mater.* 83:93–122.
- Kamogawa, M. Y., A. R. A. Nogueira, M. Miyazawa, J. Artigas, and J. Alonso. 2001. Determination of soil calcareous efficiency using flow system with pervaporative separation. *Anal. Chem. Acta* 438:273–279.
- Lagacherie, P., F. Baret, J. -B. Feret, J. M. Netto, and J. M. Robbez-Masson. 2008. Estimation of soil clay and calcium carbonate using laboratory, field and airborne hyperspectral measurements. *Remote Sens. Environ.* 112:825–835.
- Lemos, S. G., A. R. A. Nogueira, A. Torre-Neto, A. Parra, and J. Alonso. 2007. Soil calcium and pH monitoring sensor system. *J. Agric. Food Chem.* 55:4658–4663.
- Mengel, K., and E. A. Kirkby. 1978. Principles of Plant Nutrition. International Potash Institute, Bern, Switzerland.
- Potts, P. J., M. H. Ramsey, and J. Carlisle. 2002. Portable X-ray fluorescence in the characterisation of arsenic contamination associated with industrial buildings at a heritage arsenic works site near Redruth, Cornwall, UK. *J. Environ. Monit.* 4:1017–1024.
- Puffeles, M., and N. E. Nessim. 1959. Direct flame-photometric determination of calcium in soil and plant extracts, water and serum with special reference to sodium, potassium and phosphate interference. *Anal. Chem. Acta* 20:38–46.
- Rains, T. C., H. E. Zittel, and M. Ferguson. 1963. Elimination of anionic interference in the flame spectrophotometric determination of calcium. *Talanta* 50:367–374.
- Soil Survey Staff. 2004. Soil survey laboratory methods manual. Soil Survey Investigation Report No. 42. Version 4.0. USDA-NRCS. US Govt. Print. Off., Washington, DC.
- Stephens, W. E., and A. Calder. 2004. Analysis of non-organic elements in plant foliage using polarised X-ray fluorescence spectrometry. *Anal. Chim. Acta* 527:89–96.
- U. S. Salinity Laboratory Staff. 1969. Diagnosis and improvement of saline and alkali soils (revised edition). Agric. Handbook 60, USDA. U. S. Govt. Printing Office, Washington, DC.
- Ure, A. M., G. J. Ewen, and M. C. Mitchell. 1980. A three-channel flame atomic absorption/emission spectrometer for the rapid, routine determination of major cations in soil extracts and plant ash solutions. *Anal. Chem. Acta* 118:1–9.
- VanCott, R. J., B. J. McDonald, and A. G. Seelos. 1999. Standard soil sample preparation error and comparison of portable XRF to laboratory AA analytical results. *Nucl. Instrum. Methods Phys. Res., Sect. A, Accel. Spectrom. Detect. Assoc. Equip.* 422:801–804.
- Wainner, R. T., R. S. Harmon, A. W. Miziolek, K. L. McNesby, and P. D. French. 2001. Analysis of environmental lead contamination: Comparison of LIBS field and laboratory instruments. *Spectrochim. Acta, Part B: Atom. Spectrosc.* 56(7):777–793.
- Weindorf, D. C., R. Sarkar, M. Dia, H. Wang, Q. Chang, B. Haggard, A. McWhirt, and A. Wooten. 2008. Correlation of x-ray fluorescence spectrometry and inductively coupled plasma atomic emission spectroscopy for elemental determination in composted products. *Compost Sci. Util.* 16(2):79–82.
- Zouqagh, M., A. Rios, and M. Valcárcel. 2005. Direct determination of total carbonate salts in soil samples by continuous-flow piezoelectric detection. *Talanta* 65:29–35.

AUTHOR QUERIES

AUTHOR PLEASE ANSWER ALL QUERIES

AQ1 = Please check if proposed short title is ok.

AQ2 = The footnote "Please see Table 2 for symbols" was changed to indicate the expanded forms of the symbols. Please check if ok.

AQ3 = Please indicate source's academic degree and specify if communication was oral, written, or electronic.

END OF AUTHOR QUERIES

Author Reprints

For **Rapid Ordering** go to: www.lww.com/periodicals/author-reprints

Soil Science

Order

Author(s) Name _____

Title of Article _____

*Article # _____ *Publication Mo/Yr _____

**Fields may be left blank if order is placed before article number and publication month are assigned.*

Quantity of Reprints _____ \$ _____

Covers (Optional) _____ \$ _____

Shipping Cost _____ \$ _____

Reprint Color Cost _____ \$ _____

Tax _____ \$ _____

Total _____ \$ _____

Reprint Pricing

100 copies = \$375.00

200 copies = \$441.00

300 copies = \$510.00

400 copies = \$585.00

500 copies = \$654.00

Covers

\$108.00 for first 100 copies

\$18.00 each add'l 100 copies

Reprint Color

(\$70.00/100 reprints)

Shipping

\$5.00 per 100 for orders shipping within the U.S.

\$20.00 per 100 for orders shipping outside the U.S.

Tax

U.S. and Canadian residents add the appropriate tax or submit a tax exempt form.

 **Lippincott
Williams & Wilkins**
a Wolters Kluwer business

Use this form to order reprints. Publication fees, including color separation charges and page charges will be billed separately, if applicable.

Payment must be received before reprints can be shipped. Payment is accepted in the form of a check or credit card; purchase orders are accepted for orders billed to a U.S. address.

Prices are subject to change without notice.

Quantities over 500 copies: contact our Pharma Solutions Department at **410.528.4077**

Outside the U.S. call **4420.7981.0700**

MAIL your order to:
Lippincott Williams & Wilkins
Author Reprints Dept.
351 W. Camden St.
Baltimore, MD 21201

FAX:
410.528.4434

For questions regarding reprints or publication fees,

E-MAIL:
reprints@lww.com

OR **PHONE:**
1.800.341.2258

You may have included color figures in your article. The costs to publish those will be invoiced separately. If your article contains color figures, use Rapid Ordering www.lww.com/periodicals/author-reprints.

Payment

MC VISA Discover American Express

Account # _____ / _____ / _____ Exp. Date _____

Name _____

Address _____ Dept/Rm _____

City _____ State _____ Zip _____ Country _____

Telephone _____

Signature _____

Ship to

Name _____

Address _____ Dept/Rm _____

City _____ State _____ Zip _____ Country _____

Telephone _____

For **Rapid Ordering** go to: www.lww.com/periodicals/author-reprints