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Vapor Generation by UV Irradiation for Sample Introduction with Atomic Spectrometry

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Volatile species of the conventional hydride-forming elements (As, Bi, Sb, Se, Sn, Pb, Cd, Te), Hg, transition metals (Ni, Co, Cu, Fe), noble metals (Ag, Au, Rh, Pd, Pt), and nonmetals (I, S) were generated following UV irradiation of their aqueous solutions to which low molecular weight carboxylic acids (formic, acetic, propionic) had been added. Free radicals arising from photodissociation of the latter provide a new and useful alternative to the common methods of chemical/electrochemical vapor generation techniques for the determination of these analytes by atomic spectrometry. Quantitative estimates of the efficiencies of these generation processes were not undertaken, although calculated signal-to-background ratios (>1500 for 5 ng/mL As, Sb, Bi, Se, and Te; 20 for 10 ng/mL Sn, Cu, Rh, Au, Pd, Pt, and Cd; 2400 for 1 ng/mL Hg; and 1000 for Co using ICP-TOF-MS detection) do provide clear evidence of the efficacy of this approach for sample introduction. In the case of Ni and Se, the tetracarbonyl and alkylated selenium compounds have been identified, respectively.

Vapor generation sample introduction for atomic spectrometry provides a powerful detection methodology that is enjoying increasing interest for inorganic trace and ultratrace analysis because of its unmatched sensitivity, elemental specificity, and high sample introduction efficiency. It has been combined with almost every atomic spectrometry technique and is a popular component of hyphenated techniques used to achieve speciation analysis and environmental monitoring.

Reduction of metal ions to volatile forms is usually accomplished in aqueous media using various reducing agents. Apart from stannous chloride, used for reduction of mercury, sodium (or potassium) tetrahydroborate is the most frequently employed reductant (since its introduction in 1973¹). Recently, this approach has been used to further extend the scope of elements amenable to vapor generation to include Cd,^{2,3} In,⁴ Tl,^{5,6} Cu,⁷ Au, Pd, Pd,⁸

Ni,⁹ Ag,¹⁰ and Zn.¹¹ Alkylation with Grignard reagents, sodium tetraethylborate (NaBEt₄) and tetrapropylborate (NaBPr₄)¹² is also popular. The application of sodium cyanotrihydroborate(III) for generation of volatile species has been reported by D'Ulivo et al.¹³ In addition to these widely practiced techniques, the successful generation of volatile chlorides (Bi, Cd, Ge, Mo, Pb, Sn, Tl, As, Zn),¹⁴ dithiocarbamates (Cr, Fe, Zn, Co, Mn, Cu, Ni, Pd),¹⁴ and oxidation products (I, Os)^{15,16} should also be noted.

One problem common to all chemical vapor generation approaches is interferences that usually decrease sensitivity and reproducibility. Typically, these occur during the generation step, due to the coproduction of active metals that catalytically decompose NaBH₄ or adsorb and/or decompose the organometallic hydrides. In addition, the efficiency of vapor generation may depend strongly on the chemical form of the analyte in the sample, as ligands may interfere with derivatization reactions by decreasing the ability of the NaBH₄ to react with the analyte. Furthermore, NaBH₄, as well as other derivatization reagents, is expensive and a potential source of contamination.

Efforts to develop new vapor generation systems that may replace or reduce the use of chemical reagents remain fascinating. One of the first successful attempts has been the use of electrons as reductants.^{17–21} Despite apparent advantages over the use of sodium tetrahydroborate, including freedom from dependence on the oxidation state of analytes by carefully selecting the cathode material (i.e., high hydrogen overvoltage materials such as Pb or amalgamated Ag), several problems remain: the production of a reproducible solid electrode surface is not trivial; transition metal

- (8) Pohl, P.; Zyrnicki, W. *J. Anal. At. Spectrom.* **2001**, *16*, 1442–1445.
- (9) Guo, X.; Huang, B.; Sun, Z.; Ke, R.; Wang, Q.; Gong, Z. *Spectrochim. Acta, Part B* **2000**, *55*, 943–950.
- (10) Matoušek, T.; Dědina, J.; Vobecký, M. *J. Anal. At. Spectrom.* **2002**, *17*, 52–56.
- (11) Guo, X.; Guo, X. *Chin. J. Anal. Chem.* **1998**, *26*, 674–678.
- (12) De Smaele, T.; Moens, L.; Dams, R.; Sandra, P.; Eycken, J. V.; Vandeyck, J. *J. Chromatogr., A* **1998**, *793*, 99–106.
- (13) D'Ulivo, A.; Loreti, V.; Onor, M.; Pitzalis, E.; Zamboni, R. *Anal. Chem.* **2003**, *75*, 2591–2600.
- (14) Smichowski, P.; Farias, S. *Microchem. J.* **2000**, *67*, 147–155.
- (15) Yan, X.; Ni, Z. *Anal. Chim. Acta* **1994**, *291*, 89–105.
- (16) Camuña, F.; Sanchez Uribe, J. E.; Sanz Medel, A. *Spectrochim. Acta, Part B* **1993**, *48*, 1115–1125.
- (17) Rigin, V. I.; Verkhovurov, G. N. *Zh. Anal. Khim.* **1977**, *10*, 1965–1968.
- (18) Lin, Y.; Wang, X.; Yuan, D.; Yang, P.; Huang, B.; Zhuang, Z. *J. Anal. At. Spectrom.* **1992**, *7*, 287–291.
- (19) Brockmann, A.; Nonn, C.; Golloch, A. *J. Anal. At. Spectrom.* **1993**, *8*, 397–401.
- (20) Laborda, F.; Bolea, E.; Castillo, J. R. *J. Anal. At. Spectrom.* **2000**, *15*, 103–107.
- (21) Denkhaus, E.; Golloch, A.; Guo, X.; Huang, B. *J. Anal. At. Spectrom.* **2001**, *16*, 870–878.

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- (1) Schmidt, F. J.; Royer, J. L. *Anal. Lett.* **1973**, *17*, 17–23.
- (2) Sanz-Medel, A.; Valdes-Hevia y Temprano, M. C.; Bordel Garcia, N.; Fernandez de la Campa, M. R. *Anal. Chem.* **1995**, *67*, 2216–2223.
- (3) Guo, X. W.; Guo, X. M. *J. Anal. At. Spectrom.* **1995**, *10*, 987–991.
- (4) Busheina, J. S.; Headridge, J. B. *Talanta* **1982**, *29*, 519–520.
- (5) Yan, D.; Yan, Z.; Cheng, G. S.; Li, A. M. *Talanta* **1984**, *31*, 133–134.
- (6) Ebdon, L.; Goodal, P.; Hill, S. J.; Stockwell, P.; Thompson, K. C. *J. Anal. At. Spectrom.* **1995**, *10*, 317–320.
- (7) Sturgeon, R. E.; Liu, J.; Boyko, V. J.; Luong, V. T. *Anal. Chem.* **1996**, *68*, 1883–1887.

Figure 1. Schematic of the experimental system.

ions are reduced and deposited on the cathode surface altering its characteristics, and adsorption of gaseous products leads to suppression of the analytical signals.²¹

It is well known that reactive free radicals can be generated by the application of ultraviolet light. These include oxidizing species (electron acceptors or holes, e.g., the hydroxyl radical) or primary reducing agents (electron donors, such as $\text{H}^\bullet$, $\text{CO}^\bullet$, $\text{CH}_3^\bullet$), from which various stable end products or important intermediates can be formed. In the past few decades, use of oxidizing free radicals was widely utilized for the UV-assisted decomposition of organic material in samples.^{22–25} To improve upon this procedure for production of abundant oxidizing radicals (mainly $\text{OH}^\bullet$), a strong oxidizing agent, such as O_3 , $\text{K}_2\text{S}_2\text{O}_8$, $\text{K}_2\text{Cr}_2\text{O}_7$, HNO_3 , or H_2O_2 , is often added to the system.

In contrast to oxidation, the formation of volatile mercury species by photochemical processes serves as a typical example of the application of free radicals for the purpose of reduction.^{26,27} Kikuchi and Sakamoto²⁸ reported the formation of volatile species of selenium (presumably SeH_2) when photolyzing aqueous solutions fortified with formic acid in the presence of TiO_2 photocatalyst. Photochemical reduction of chromium(VI) by alcohols was reported by Mytych et al.²⁹ and selenium hydride, selenium carbonyl, dimethyl selenide, and diethyl selenide can be generated by exposure of aqueous inorganic selenium(IV) solutions to UV irradiation in the presence of low molecular weight organic acids.³⁰ Volatile nickel tetracarbonyl $\text{Ni}(\text{CO})_4$ is formed from inorganic nickel solutions under similar conditions.³¹ Despite such studies, little is known in this area as not much effort has been expended in clarifying UV “photoreduction” reactions to permit their routine use in analytical chemistry.

Table 1. ICP-TOF-MS and ICP-OES Operating Conditions

ICP-TOF-MS	
rf power (27.12 MHz)	1200 W
plasma gas flow rate	10 L min^{-1}
auxiliary gas flow rate	0.60 L min^{-1}
nebulizer gas flow rate	0.65 L min^{-1}
ICP-OES	
rf power	1150 W
plasma gas flow rate	15 L min^{-1}
auxiliary gas flow rate	0.5 L min^{-1}
carrier gas flow rate	0.35 L min^{-1}

Development of a new vapor generation technique based on UV irradiation is described in this study that is applicable to a wide range of elements, including conventional hydride-forming elements (As, Bi, Sb, Se, Te, Pb, Sn), Hg, transition metals (Ni, Co, Cu, Fe), noble metals (Ag, Au, Rh, Pd, Pt), and nonmetals (I, S).

EXPERIMENTAL SECTION

Reagents and Samples. All solutions were prepared using 18 $\text{M}\Omega\cdot\text{cm}$ deionized, reverse osmosis water (DIW) obtained from a mixed-bed ion-exchange system (NanoPure, model D4744, Barnstead/Thermoline, Dubuque, IA). Working solutions were prepared daily by diluting 1000 mg L^{-1} stock solutions of As(III), Sb(III), Bi(III), Se(IV), Te(IV), Sn(IV), Pb(IV), Cd(II), Hg(II), Fe(III), Ni(II), Co(II), Cu(II), Ag(I), Au(III), Pt(II), Pd(II), Rh(III), I(I), and S(VI). Solutions of low molecular weight acids (LMW) were prepared from analytical reagent grade materials: formic acid (23 M, Anachemica), acetic acid (6.3 M, BDH), and propionic acid (13 M, BDH). High-purity HNO_3 and HCl (Fisher Scientific) were used for solution acidification, except where indicated otherwise.

Instrumentation. An Optimass 8000 ICP-TOF-MS instrument (GBC Scientific Equipment Pty. Ltd.) was used; operating parameters are given in Table 1. A schematic of the experimental system is presented in Figure 1. The following isotopes were monitored: ^{75}As , $^{121,123}\text{Sb}$, ^{209}Bi , $^{78,82}\text{Se}$, $^{126,128,130}\text{Te}$, $^{116,118,120}\text{Sn}$, $^{206,207,208}\text{Pb}$, $^{110,112,114}\text{Cd}$, $^{200,201,202}\text{Hg}$, $^{58,60}\text{Ni}$, ^{59}Co , $^{63,65}\text{Cu}$, $^{107,109}\text{Ag}$, ^{197}Au , $^{194,195,196}\text{Pt}$, $^{105,106,108}\text{Pd}$, ^{103}Rh , and ^{127}I .

An IRIS axial view ICP-OES spectrometer (Thermo Jarrell Ash Corp., Franklin, MA) equipped with an echelle grating polychro-

- (22) Golimowski, J.; Golimowska, K. *Anal. Chim. Acta* **1996**, *325*, 111–133.
- (23) Low, G. K.-C.; Meevov, S. R. *Trends Anal. Chem.* **1996**, *15*, 151–156.
- (24) Lores, M.; Cabaleiro, O.; Cela, R. *Trends Anal. Chem.* **1999**, *18*, 392–400.
- (25) Tsalev, D. L.; Sperling, M.; Welz, B. *Spectrochim. Acta, Part B* **2000**, *55*, 339–353.
- (26) Akagi, H.; Fujita, Y.; Takabatake, E. *Chem. Lett.* **1976**, *49*, 1–4.
- (27) Hayashi, K.; Kawai, S.; Ohno, T.; Maki, Y. *J. Chem. Soc., Chem. Commun.* **1977**, 158–159.
- (28) Kikuchi, E.; Sakamoto, H. *J. Electrochem. Soc.* **2000**, *147*, 4589–4593.
- (29) Mytych, P.; Karocki, A.; Stasicka, Z. *J. Photochem. Photobiol., A* **2003**, *160*, 163–170.
- (30) Guo, X.; Sturgeon, R. E.; Mester, Z.; Gardner, J. G. *Anal. Chem.* **2003**, *75*, 2092–2099.
- (31) Guo, X.; Sturgeon, R. E.; Mester, Z.; Gardner, J. G. *Appl. Organomet. Chem.*, in press.

mator and CID detector was employed for the determination of Fe and S, as ICPMS is not suitable for detection due to serious interferences. The operating conditions for this instrument are also summarized in Table 1.

Photoreduction was accomplished using a 100-mL septum-sealed glass batch reactor (20 cm diameter $\times$ 30 cm depth) as illustrated in Figure 1. Sample solutions containing the analytes were irradiated with a UVC pen lamp (Analamp, Claremont, CA, $79 \mu\text{W cm}^{-2}$, λ_{max} 253.7 nm) inserted into a quartz finger (12-mm o.d., 10-mm i.d., 11.5-cm depth) positioned at the center of the reactor such that it was effectively immersed in the analyte solutions but isolated from direct contact with the liquid medium.

Argon carrier gas was used to mechanically sparge gaseous products from the reactor and to maintain the solution at $30 \pm 5^\circ\text{C}$. Optimum flow rates for sample sparging were between 20 and 100 mL min^{-1} and were selected based on maximum response. An additional flow of 1 L min^{-1} Ar was introduced into the system via a "T" joint to maintain the plasma.

Procedure. Every irradiation step was preceded by at least a 20-s purge with Ar to ensure that constant ICPMS response was obtained and that subsequent reactions occurred under oxygen-free conditions. A blank response was measured before every analytical run using solutions containing only the LMW acids. No detectable analytes were found for any element studied. "Dark" experiments were performed using an aluminum foil-wrapped lamp, wherein the test solutions received no UV radiation, so as to verify that no volatile species were generated as a consequence of thermal effects.

RESULTS AND DISCUSSION

Most elements tested produced a very low signal during the initial 10 s of irradiation, after which response increased rapidly and thereafter either decreased almost exponentially or remained constant. The generation of volatile species was completely dependent on the presence of UV light. For many elements, response ceased immediately after the UV lamp was turned off or decreased very slowly for others, suggesting that generation may involve at least three steps: reduction of the ions to their low oxidation state, formation of volatile compounds, and their transfer to the gas phase. For some elements, such as Te, Hg, and I, these steps occur very rapidly, whereas for others, these processes occur more slowly, resulting in significant tailing of signals after the UV source is turned off. No measurable signals could be obtained when reagent blanks were being processed.

The elements selected for study were arbitrarily grouped into several subsets in an effort to facilitate discussion of the results. This should not be construed as an attempt to convey any classification based on reaction mechanism or product identity.

Generation of Volatile Species of As, Sb, Bi, Se, and Te.

Initial experiments with UV vapor generation were undertaken with As, Sb, Bi, Se, and Te; typical results are reported in Figures 2 and 3. Sample acidities were chosen after taking into account the range of acidity giving maximum yield in the generation process. Volatile species were readily produced from all of these elements. Compared to the formic acid system, acetic acid was optimal for generation of volatile arsenic and antimony compounds whereas propionic acid was best for bismuth and tellurium. The UV irradiation time for production of volatile species from each element varied with the acid used, suggesting that the resultant

Figure 2. (a) Transient response obtained for photochemical vapor generation of As from solutions spiked with 5 ng/mL As(III) and containing low molecular weight organic acids: I, 4.6 M formic acid; II, 3.2 M acetic acid; III, 6.5 M propionic acid. (b) Transient response obtained for photochemical vapor generation of Ag from a solution spiked with 10 ng/mL Ag(I) and containing 2.3 M HCOOH + 1.6 M CH_3COOH . (c) Transient response obtained for photochemical vapor generation of Cd from solutions spiked with 10 ng/mL Cd(II) and containing low molecular weight organic acids: I, 4.6 M formic acid; II, 3.2 M acetic acid.

molecular species may be different. For example, in the case of arsenic, a very sharp signal (although much weaker in intensity in comparison with that arising with other acids) could be produced with irradiation times as short as 20 s, and the entire reaction could be completed in 40 s in a formic acid solution. However, longer than 300 s, and 400 s for appearance of a signal, and at least 20 min and more than 30 min for completion of the reactions, were needed when acetic and propionic acids were used, respectively. This implies that the species produced with formic acid is more volatile than those formed with the other LMW acids. The ease of vapor generation for individual elements appears to decrease in the order Te(IV), Sb(III), As(III), and Bi(III). For a sample volume of 40 mL and a concentration of 5 ng/mL of As(III)

Figure 3. Photochemical vapor generation of ^{123}Sb and ^{130}Te from a solution spiked with 5 ng/mL Sb(III) and Te(IV) and containing varying concentrations of $\text{CH}_3\text{CH}_2\text{COOH}$: Te I, 0.13 M; II, 0.026 M; and Sb III, 0.13 M; IV, 0.026 M.

and Te(IV) in a propionic acid system, the entire reaction was completed within 7 min for Te, whereas more than 30 min was required for Bi. More interesting results were obtained with the reduction of tellurium and antimony, as their volatilization is markedly dependent on solution acidity (cf. Figure 3). In 0.13 M propionic acid, the signal for Sb appeared immediately after the complete release of Te from the solution, whereas in 0.026 M propionic acid, formation of volatile species of Sb could be delayed for 7 min without affecting response from Te. This difference in reaction kinetics could provide a potential separation capability for analytical applications. The conditions for Se vapor generation under UV irradiation are very similar to those for As, as demonstrated in previous studies.³⁰ Signal-to-background ratios calculated from isotope intensities were estimated under optimal generation conditions. Values of 2400, 2300, 2000, 1400, and 1500 for 5 ng/mL solutions of As(III), Sb(III), Bi(III), Se(IV), and Te(IV), respectively, were obtained.

Generation of Volatile Species of Sn, Pb, Cd, and Hg. The acidity required to generate hydrides of tin and lead is critical, and oxidation reagents are frequently used for the reduction of lead in conventional vapor generation systems.³² With this in mind, it is surprising that volatile species can be produced from these elements using simple UV irradiation. Our results provide strong signal intensities following irradiation of 40-mL solutions of 10 ng/mL Sn and Pb containing various LMW acids. In contrast to results for As, Sb, and Te described above, the intensities of the Sn and Pb signals are comparatively low and sharp peaks are difficult to obtain, indicating that the reactions are slow and the efficiency poor. More interesting results arise with cadmium which, in contrast to the elements of groups V and VI, readily produces a very sharp signal response even in formic acid solution (cf. Figure 2c). However, a more effective reaction appears to occur in an acetic acid medium, wherein the intensity of the Cd signal is similar in peak height but larger in peak area than that obtained with formic acid. The signal-to-background intensity ratios calculated under optimum generation conditions are 18, 350, and 17 for 10 ng/mL solutions of Sn(IV), Pb(IV), and Cd(II), respectively.

Photochemically produced mercury species are not new. In the presence of acetate ion or acetic acid, Hg^{2+} gives rise to

Figure 4. Photochemical vapor generation of 1 ng/mL Hg(II) from a solution containing I, 2.3 M formic acid; II, 1.3 M acetic acid; III, 1.7 M propionic acid; response from 10 ng/mL iodine generated from a solution containing IV, 2.6 M $\text{CH}_3\text{CH}_2\text{COOH}$.

methylmercury following UV photolysis.^{26,27} It has also been reported that photolysis of aliphatic α -amino acids in the presence of mercury(II) chloride results in the formation of methylmercury.²⁷ The product yield and time required (more than 3–4 h) for generation of methylmercury are not attractive for analytical applications. In the present case, results for reduction of mercury in the presence of various LMW acids are summarized in Figure 4. In all cases, sharp peaks were easily obtained and the entire reaction could be completed within 2 min. The signal-to-background intensity ratio under optimal conditions is 2400 for a 1 ng/mL solution of Hg(II). This may be contrasted with the data for silver, presented below.

Generation of Volatile Species of Transition Metals. The ICP-OES signal intensity for Fe increased very slowly with change in irradiation time, but a very strong signal was evident at the 238.2-, 239.5-, and 259.9-nm lines. Apart from Fe, Cu was also detected. Significant noise was present in these signals, implying that the resulting volatile compounds are unstable and easily decomposed during transport to the plasma. Unlike Cu, formation of $\text{Ni}(\text{CO})_4$ was very easily achieved, with a generation efficiency of more than 95%.³¹ Similar results were obtained with solutions of cobalt, although the signal did not spike but continuously increased with irradiation time, implying that the reaction is relatively slow. It is likely that the resultant volatile product is, by analogy to nickel, cobalt carbonyl. The signal-to-background intensity ratios estimated under optimum conditions are 16, 1000, and 160 for 10 ng/mL solutions of Cu(II) and 5 ng/mL solutions of Co(II), and Ni(II), respectively.

Generation of Volatile Species of the Noble Metals. Ions of the noble metals, such as gold, silver, and platinum, as well as mercury, have high electrochemical potentials and are easily reduced but tend to precipitate. Once accomplished, the pillar and pore architectures of these microparticles or metal colloids allow strong redox gradients to be formed, further promoting the reduction to yield products by combining with $\text{H}^\bullet$, $\text{CO}^\bullet$, and $\text{CH}_3^\bullet$ radicals. Relatively strong ICPMS signal transients are readily generated from 10 ng/mL solutions of Au, Ag, Pt, Rh, and Pd. Among them, Ag and Rh appear useful for vapor generation sampling with good efficiency (cf. Figure 2b). However, the very noisy signals again imply that the compounds formed are unstable. The signal-to-background intensity ratios estimated under optimal

(32) Dedina, J.; Tsalev, D. L. *Hydride Generation Atomic Absorption Spectrometry*; Wiley and Sons: New York, 1995.

conditions are 170, 28, 16, 27, and 10 for 10 ng/mL solutions of Ag(I), Rh(III), Au(III), Pd(IV), and Pt(III), respectively.

Generation of Volatile Species of Nonmetals (I, S).

Although the sensitivity for detection of sulfur by ICP-OES is poor, strong intensities at 180.7 and 182.0 nm were obtained, indicating that volatile sulfur species were produced during UV irradiation. Because the OES signal intensity increased significantly after the sulfur-containing solutions were subjected to a long purge with Ar, it was believed that pretreatment of the solution to remove soluble oxygen prior to UV irradiation is important. This result suggests that photochemical production of several sulfur-containing species may occur, including SO_2 , H_2S , COS, and $\text{S}(\text{CH}_3)_2$. This situation is quite similar to that noted for selenium, in which H_2Se , COSe, and $\text{Se}(\text{CH}_3)_2$ are major reaction products, depending on the LMW acid used.³⁰ It was noteworthy that, except for mercury, iodine is very easily transformed to a volatile form from its ionic state. The volatile species can be generated using irradiation times as short as 2–5 s. Figure 4 (IV) illustrates typical response for generation from solutions spiked with 10 ng/mL iodide. Although iodide can be oxidized to I_2 in acidified solutions using $\text{K}_2\text{S}_2\text{O}_8$, KMnO_4 , or H_2O_2 ,^{15,33,34} the standard potential (E^{06}) for the half-reaction ($\text{I}_2 + 2\text{e}^- = 2\text{I}^-$) is 0.536 V, suggesting that it is not easy to oxidize iodide, especially in the absence of such oxidizing agents. Similar to sulfur, iodide may follow either a

photochemical oxidation pathway to yield I_2 or produce the carbonyl, methyl, or ethyl compounds by direct radical cleavage. Clearly, work is required to deduce the actual reactions and product identities. Nevertheless, the fact that volatile species of nonmetals form, significantly enlarges the scope of application of UV vapor generation, making it a fascinating research topic. The signal-to-background intensity ratios estimated under optimal conditions are 1300 for a 10 ng/mL solution of iodide and 200 for a 5 μg /mL solution of S(VI) (as the SO_4^{2-}).

CONCLUSION

UV vapor generation may prove to be a useful new alternative to the commonly employed wet chemical and electrochemical hydride generation techniques. Significant additional work is required not only to identify the nature of the resultant species but to find conditions under which maximum yield occurs to identify interferences and to delineate the full scope of application.

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(33) Duan, Y.; Wu, M.; Jin, Q.; Hieftje, G. M. *Spectrochim. Acta, Part B* **1995**, *50*, 1095–1108.

(34) Nakahara, T.; Mori, T. *J. Anal. At. Spectrom.* **1994**, *9*, 159–164.