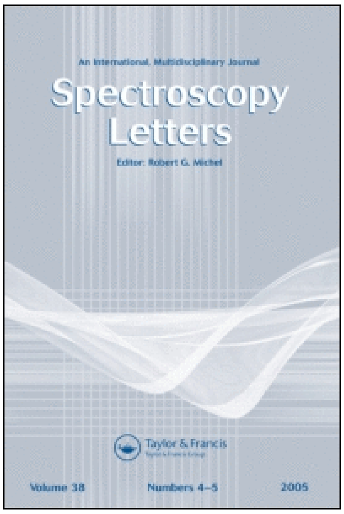

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THE DETERMINATION OF MERCURY IN SILVER BY LASER-EXCITED ATOMIC FLUORESCENCE SPECTROMETRY WITH ELECTROTHERMAL ATOMIZATION

KEY WORDS: mercury, silver, atomic fluorescence spectroscopy, laser excitation, electrothermal atomization

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ABSTRACT

This work shows that laser excited atomic fluorescence spectrometry, LEAFS, combined with electrothermal atomization, ETA, is useful for the determination of trace concentrations of mercury in small amounts of silver metal. Only minimal sample preparation procedures, such as dilution of very concentrated solutions and digestion of solid samples, are necessary. The practical limit of detection for this work is found to be blank limited, 50 pg/ml, and the instrumental limit of detection was laser scatter limited at 7 pg/ml.

INTRODUCTION

LEAFS-ETA with a two-color excitation scheme, has been shown to be highly selective for the direct determination of mercury.[1,2] Observation of fluorescence at a wavelength greater than either laser excitation wavelength provided excellent LODs and LDRs. Therefore, the detection of trace amounts of mercury in a matrix, such as silver, is possible and only small amounts of the silver sample are needed.

Since the advent of photography in 1839, mercury has played an important role in photographic development. Because mercury is a photosensitive element, and can influence the image formation process, it is important to analyze it at very low levels in silver-based photographic chemicals.

The determination of trace quantities of mercury in silver has been an arduous task due to the amalgamation characteristics of mercury with silver.[3] Most successful methods have consisted of complicated procedures or have given inconsistent, unreliable results. A colorimetric method for mercury in high purity silver involved concentrating the mercury in a silver iodide precipitate.[4] However, this method was quite complex and required 10 g of sample to detect 600 ng of mercury. A simpler method was developed by White and Murphy[3] in which mercury was separated from silver as $HgBr_4^{2-}$ complex. The insoluble silver bromide was filtered leaving the mercury complex in the filtrate, which was determined using atomic absorption spectrometry. However, it was found that this method was unsatisfactory for the lower levels of mercury encountered.[5] The recovery was erratic, presumably caused by coprecipitation of mercury in the silver bromide.

Direct determination of mercury by conventional atomic fluorescence spectrometry (AFS) or atomic absorption spectrometry (AAS) is not sufficiently sensitive to monitor ng/ml levels of mercury.[6] However, the limits of detection are improved by combining them with preconcentration techniques before the final measurement of mercury. Amalgamation with metals such as copper wire,[7] silver wool,[8] and gold foil,[5,8-10] have significantly improved the detection limits. Many of these publications involve the determination of mercury in water and biological systems. All of these collection devices and detection schemes resulted in detection limits of 100 ng/ml or worse.

Although the methods described above were efficient in collecting mercury, they lacked the detection limits required for trace analysis of mercury in photographic silver. The photographic industry desires essentially "mercury-free" silver for their processing, and only those methods with limits of detection in the pg/ml range are useful. Laser excited atomic fluorescence spectroscopy with electrothermal atomization (LEAFS-ETA) is an excellent analytical technique for determining trace impurities in both solids and aqueous solutions.[11-19] The main advantages of LEAFS are the extremely low limits of detection, the wide linear range of the calibration curve, the high analytical selectivity, and the comparative simplicity of the technique. LEAFS is capable of analyzing samples of complex compositions. LEAFS has been combined with sample atomization in an inert atmosphere in a carbon ETA, resulting in limits of detection (LOD) down to the parts per trillion level.[1,2,11-19]

LEAFS-ETA has been used for the determination of lead in sea-waters; a detection limit of 1 pg/ml was reported.[20] LEAFS-ETA has also been used for the detection of selenium and arsenic in aqueous solutions in samples of human whole blood;[21] detection limits of 1.5 pg/ml for selenium and 5.4 pg/ml for arsenic were obtained, linear dynamic ranges spanned six orders of magnitude and good precision was achieved, despite the difficult matrix of blood. Absolute detection limits for aqueous mercury solutions using LEAFS-ETA have been reported as low as 60 fg[1] and 90 fg.[2]

The goal of this research was the application of LEAFS-ETA to the determination of low level concentrations of mercury in silver. Digested silver samples were introduced directly into a graphite furnace and subsequently atomized. The number density of mercury atoms in the probed vapor volume (10 µL) was large enough for mercury fluorescence to be detected in a silver matrix and preconcentration was unnecessary.

EXPERIMENTAL

Instrumental System

The instrumental system, shown in Figure 1, is identical to the one used by Resto, et al[2] and by Pagano, et al.[1] In brief, the system consisted of a Questek XeCl excimer laser (71 mJ/pulse, 20 Hz) which pumped two Molectron dye lasers producing 507.4 nm (3.75 mJ) and 435.8 nm (0.75 mJ), respectively. The 507.4

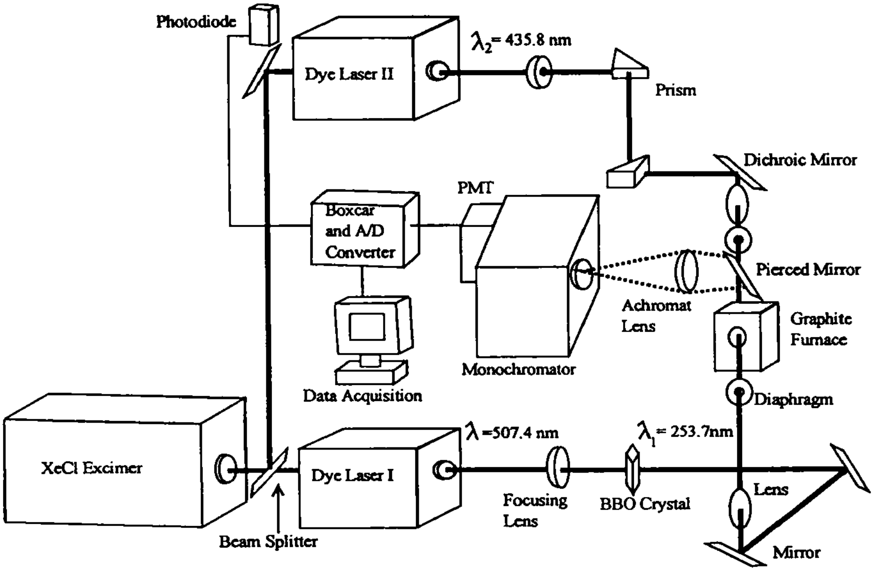

FIG. 1 Schematic of the instrumental set-up for LEAFS-ETA.

nm radiation was frequency doubled to 253.7 nm (300 μJ) using a BBO crystal. A Perkin-Elmer HGA-400 electrothermal atomizer with pyrolytically coated graphite tubes and L'Vov platform were used for all studies.

A Pellin Broca prism, which would have provided a greater second harmonic generation efficiency, was initially used to separate the second harmonic (253.7 nm) from the fundamental (507.4 nm). However, the detection system was not protected from the large amounts of 507.4 nm radiation scattered off the prism surfaces, reflections from the walls, etc. With an increase in the background noise, the signal to noise ratio for the Pellin Broca prism was low. Therefore, simple filtration with a UG-5 filter was used to reduce the amount of scatter as well as the background signal and to enhance the S/N.

Both laser beams (λ_1 and λ_2) were directed into the center of the graphite tube. Care was taken to avoid reflections off the graphite tube walls. The window mounts on each side of the atomizer was tilted to minimize collection of reflected laser radiation.

The fluorescence inside the furnace was collected by front-surface illumination of the pierced, plane mirror as described by Wei, et al.[22] The pierced mirror was located on the side closest to λ_2 (435.8 nm) and was placed at a 45° angle with respect to the excitation axis. The pierced mirror reflected the fluorescence to a lens (10 cm focal length, f/2) placed between the furnace and the monochromator. The width of the entrance and exit slit widths on the double monochromator (22 cm focal length, f/4, 500 nm blazed gratings) were 3 mm. Black baffles were used to minimize blackbody radiation from the graphite tube entering the monochromator. In addition, a quartz cell with K_2CrO_4 (8.1 g/cm^3) was placed between the lens and the monochromator entrance slit to absorb 253.7 nm and 435.8 nm radiation while transmitting (94%) the fluorescence at 546.1 nm.

In the two-color excitation scheme, the simultaneous arrival of laser pulses at the two wavelengths was essential. Therefore, timing was assured using a delay line in one of the beams and monitoring the laser pulse scatter within the graphite furnace. A repetition rate of 20 Hz was used for all studies. This was a compromise between laser pulse energy which decreased with repetition rate and total signal which increased to a plateau with repetition rate. Repetition rates of 20 Hz and below prolonged the lifetime of the excimer fill gas. The fluorescence was detected by a 1P28 photomultiplier tube operated at -950 V. The output from the photomultiplier was terminated with a 1200 Ω resistor and sent to a Stanford boxcar integrator. The boxcar was externally triggered (using a photodiode) by excimer laser scatter. The output of the boxcar was sent to an analog-to-digital converter.

Standard Preparation and Procedure

Mercury standards were prepared in a clean hood to reduce contamination by dust particles in the air. Several dilutions of 1000 μg/ml stock mercury solution (mercuric nitrate in 1.8% nitric acid) with 1.05% nitric acid produced solutions of various concentrations. Seastar nitric acid (<0.1 ppb Hg) and ultrapure deionized water (Millipore, resistivity of 18.2 MΩ·cm) were used in the preparation of all solutions. All glassware had been previously cleaned using 20% nitric acid and ultrapure deionized water. Standards were stored in 30 ml narrow-mouthed PTFE bottles. Caps remained on all bottles except for the instant of removing the sample for measurement.

All solutions (10 μL) were introduced into the graphite tube furnace with an Eppendorf pipette (Fisher Scientific) using Fisherbrand Redi-Tips which were certified to have a maximum mercury level of 0.2 ng/tip.

Preparation of Silver Metal Samples

The silver samples used were of unknown origin and varied in both size and shape. Some pieces of silver were chips of metal, some metal shavings, while others more crystalline in structure. Silver metal samples were digested in 2 ml of a 50:50 volume to volume mixture of high purity nitric acid and ultrapure deionized water. Most pure silver samples readily dissolved in acidic solutions; however the silver samples used here did not. The temperature of the solutions were increased to 40 °C if the dissolution rate seemed low. After dissolution, the solution were diluted with ultrapure deionized water. This final dilution brought the nitric acid concentration to 1.05% which was consistent with the mercury standards used to construct the calibration curve. In addition, the lower acid concentration minimized degradation of the furnace.

Instrumental and Sampling Procedure

Prior to measurements in the graphite tube furnace, a quartz cell containing mercury vapor was inserted in the beam path near the furnace and used for wavelength tuning of the two laser beams (λ_1 and λ_2). Optimal tuning was achieved by detecting the maximum fluorescence signal from the cell. Nine different standards (100 pptr to 10 ppm Hg) were measured as well as a blank (1.05% nitric acid). The sampling procedure was similar to the ones used by Resto, et al[2] and Pagano, et al.[1] First, the matrix modifier (10 μL of 1000 ppm palladium chloride) was introduced to the graphite tube, dried for 60 s at 130 °C using a ramp time of 5 s. The modifier was then heated to 1300 °C for 10 s, and the furnace was allowed to cool to room temperature requiring 45 s. Second, a 10 µL aliquot of the standard or sample was introduced into the furnace, and the furnace was ramped for 5 s up to 130 °C, where the temperature was maintained for 60 s. Third, the mercury was atomized at 1400 °C for 10 s using the maximum ramp rate. Argon continuously flowed except during the mercury atomization step. Finally, the furnace was heated to 2000 °C for 5 s to clean the graphite tube. Data was taken during the 10 s atomization step.

Data Analysis

All signals were taken as the net signal minus the area of the blank (1.05% nitric acid) signal. The limit of detection was based on a signal to blank standard deviation of 3.

Mercury Excitation and Fluorescence Transitions

In Figure 2, the two excitation steps and the three possible fluorescence steps are shown. Resto[2] demonstrated that the limit of detection (LOD) for the 546.1 nm fluorescence line was the best of those fluorescence transitions shown in Figure 2 and had a linear dynamic range (LDR) of at least five orders of magnitude. The LDR at 546.1 nm was limited at high concentrations where a cooperative effect (amplified spontaneous emission, ASE) occurred and a collimated beam of stimulated fluorescence emerged from the furnace. ASE is due

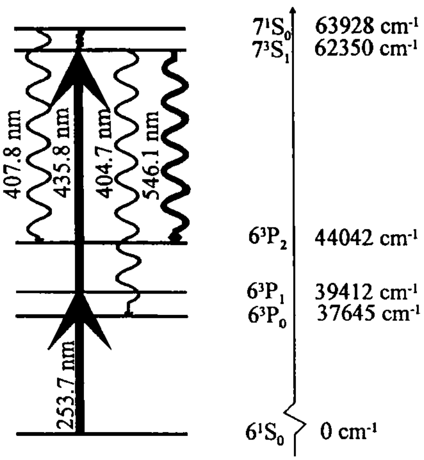

FIG. 2 Partial energy diagram of mercury.

to an inversion of the population that occurs from the levels involving the 546.1 nm and the 404.7 nm transitions during the excitation pulse. The LDR could be extended to at least seven orders of magnitude by resorting to fluorescence measurements at the collisionally coupled transition at 407.8 nm where no inversion of population occurs. For this research, it was more important to have a lower limit of detection than a wider LDR. Consequently, in this study, the fluorescence from the 546.1 nm transition was measured.

Saturation plots of fluorescence signal versus laser energy were performed at λ_1 (laser at λ_2 constant in energy/pulse) and at λ_2 (laser at λ_1 constant in energy/pulse). In both cases, the fluorescence was saturated at laser energies below the maximum available.

RESULTS AND DISCUSSION

Gas Conditions During Atomization

Three different argon flow conditions[23] were evaluated for the furnace: in normal flow, a continuous stream of argon passed through the furnace chamber; in stop flow, the argon gas flow was stopped during the mercury atomization; in mini-flow, the rate of argon gas flow was reduced during atomization. The relative signal level by the stopped flow mode was 20 times greater than the normal flow and 30 times greater than the mini-flow. Thus, stopped flow conditions were used in all cases.

Furnace Temperature

Temperatures ranging from 100 to 1800 °C were evaluated. If the temperature was above 1400 °C, the emission background noise increased, and if below 1400 °C, the fluorescence signal decreased. Similarly, the best drying temperature was found to be 130 °C for 1 minute. Although mercury atomization should occur at 1200 °C, with atomization temperatures below 1400 °C, the mercury fluorescence contained a major peak with a shoulder. At 1400 °C, the shoulder disappeared.

Mercury Contamination

During these studies, a significant source of mercury contamination was noted. With considerable effort, it was shown that the source of the mercury contamination was not the PTFE bottles as long as proper cleaning and handling procedures were used and was not the pipette tips as long as the high purity tips were used. The ultrapure deionized water was also not the source of contamination. The major source of contamination was found to be the graphite tube holders of the HGA-400 furnace.

Mercury from previous samples condensed on the holders and then vaporized during the atomization steps of the latter samples. When the electrodes were removed, cleaned, and replaced, the background mercury signal dropped to the blank level.

Analytical Calibration Curve

In Figure 3, the LEAFS-ETA calibration curve for mercury is given. The IUPAC limit of detection (LOD) is found to be 0.07 pg or 7 pptr. The blank limited detection limit is 0.5 pg or 0.05 ppb. The linear dynamic range (LDR) extends over at least 7 orders of magnitude.

Silver Sample Analysis

Ten different solid silver samples were analyzed for mercury. In Table 1, the results are given for the 10 samples. As can be seen from these results, the silver in samples 8, 9, and 10 was at or below the LOD. Because of the amount of samples available and the low concentrations of mercury, it was not possible to corroborate the values given in the final column for samples 1-7. It was also found that the sizes and shapes of the crystals did not have any effect on the amount of mercury detected.

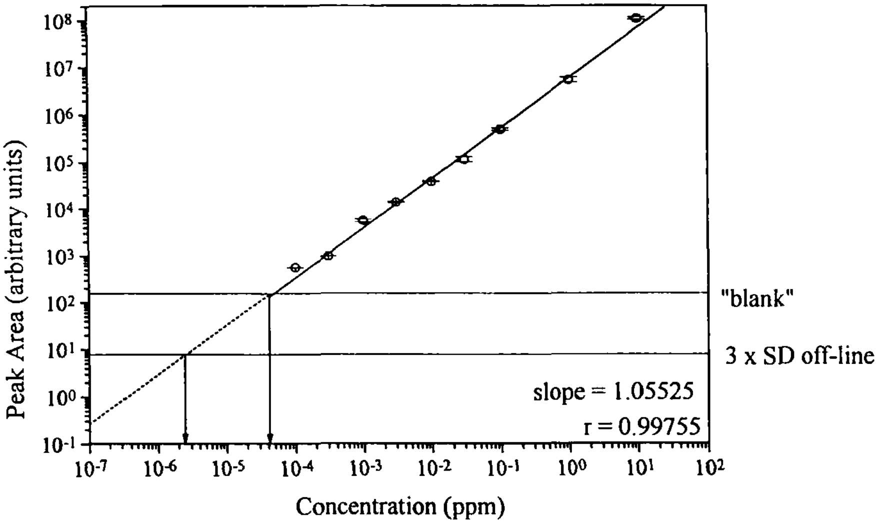

FIG. 3 Calibration curve for mercury fluorescence at 546.1 nm.

Table 1
Concentration of Mercury in Various Silver Samples

Silver Sample	g Ag in 2 ml of 50/50 HNO_3/H_2O	Blank[a]	[Hg][b] (pg/ml)	[Hg] in Ag (ng/g)
1	0.2477	1	140 ± 47	34 ± 12
2	0.0876	2	210 ± 67	154 ± 5
3	0.0363	3	120 ± 39	91 ± 3
4	0.0148	3	60 ± 20	112 ± 37
5	0.0231	3	510 ± 160	612 ± 192
6	0.0398	4	28 ± 9.5	19 ± 7
7	0.0430	4	190 ± 61	122 ± 39
8[c]	0.0523	3	5.7 ± 3.5	~LOD
9[c]	0.1093	2	5.6 ± 3.5	~LOD
9	0.0554	3	< LOD	< LOD
10	0.2449	3	< LOD	< LOD
10	0.1806	1	< LOD	< LOD

[a] Concentration (ppb) of mercury in 10 μL of blank ± standard deviation (ppb).
blank 1 2 ± 1; blank 2 5 ± 2; blank 3 1 ± 0.5; blank 4 1 ± 0.3

[b] Values do not include mercury contribution from the blank.

[c] The high % RSD for these values suggests that they are indistinguishable from the blank and therefore contain no detectable mercury.

To verify the results for mercury determination using LEAFS-ETA, the NIST mercury in water standard was analyzed. A calibration curve with mercury standards was constructed and the NIST standard was treated as an unknown. The analysis of the NIST mercury in water standard (certified concentration of 1.47 μg/ml) was experimentally determined to have a mercury concentration of 1.3 ± 0.21 μg/ml, indicating that the LEAFS-ETA measurement procedure was accurate.

FUTURE WORK

Although the absolute limit of detection for the LEAFS-ETA technique is in the low picogram range, there is still room for improvement. The background noise is high but can be reduced. Studies with an oscilloscope show that the 435.8 nm radiation is the primary cause of background noise because of reflection off the furnace window's surface and reflection by the pierced mirror towards the monochromator. Relocating the pierced mirror to the 253.7 nm beam side should reduce the collection of the reflected radiation of 435.8 nm. The 253.7 nm radiation does provide some background noise, but it is significantly less and the spot size is much smaller making it easier to pass cleanly through the pierced mirror.

In order to decrease the blank limit which presently is the limiting factor, several improvements may be made. During the course of this work, it was found that the holders for the graphite furnace were contaminated by mercury. New holders should frequently be exchanged and the graphite tube should be changed as well.

Another interesting detection scheme would be one-color excitation at 253.7 nm and detection of the fluorescence at the same wavelength. The long lifetime of this excited level would allow for possible discrimination of the laser scattering by proper time delay of the boxcar averager gate.

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