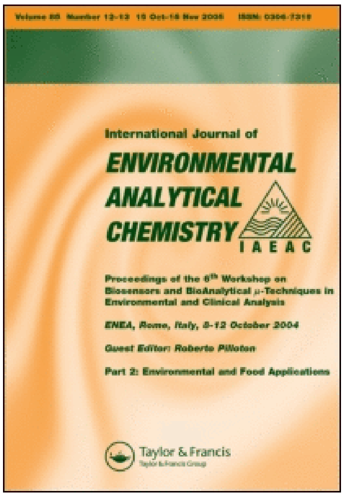

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Halldór Ármannsson[a][b]; Peter J. Ovenden[a]
[a] Department of Oceanography, The University, Southampton, England [b] Geothermal Division, Qrkustofnun, The National Energy Authority, Reykjavik, Iceland

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The Use of Dithizone Extraction and Atomic Absorption Spectrometry for the Determination of Silver and Bismuth in Rocks and Sediments, and of a Demountable Hollow Cathode Lamp for the Determination of Bismuth and Indium

HALLDÓR ÁRMANNSSON† and PETER J. OVENDEN
Department of Oceanography, The University, Southampton SO9 5NH, England

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A method involving dithizone extraction and atomic absorption spectrometry is presented for the determination of silver and bismuth in rocks and sediments. Flame atomization is used for silver, but graphite furnace atomization for bismuth. A demountable hollow cathode lamp with exchangeable hollow cathodes was used in the bismuth determination, and also for indium measurements. Bismuth and silver have been determined in three USGS rock reference samples and satisfactory agreement with listed data found. Data on silver concentrations in sediments from various locations are presented.

KEY WORDS: Silver, bismuth, indium, rocks, sediments.

INTRODUCTION

The determination of several metals in rocks, sediments, sea water and biological tissues, employing dithizone extraction and a.a.s., has been

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†Present address: Geothermal Division, Orkustofnun, The National Energy Authority, Grensásvegur 9, 108 Reykjavik, Iceland.

described by one of the authors.[1,2] A mixture of hydrofluoric, sulphuric and perchloric acids was recommended for the digestion of sediments. In subsequent work it was found that this method was unsuitable for calcium-rich sediments since an insoluble residue (probably CaF_2 or $CaSO_4$) persisted. An alternative procedure, utilizing hydrochloric acid was developed and is recommended for calcium-rich sediments.

Flame a.a.s. was not sensitive enough for the determination of bismuth and indium in rocks,[3] but was successfully employed for the determination of silver. The background absorption was steady and scale expansion could be used to advantage. Bismuth and indium are relatively uncommon metals[3] and neither is considered toxic,[4] so the need for their routine determination is unlikely to arise. In such circumstances a demountable hollow cathode lamp with interchangeable cathode has proved useful as it obviates the need to purchase individual lamps whilst extending the range of elements which can be determined, by the analyst, at relatively low cost. The lamp used in the present work for bismuth and indium is described below.

THE CONSTRUCTION OF THE DEMOUNTABLE HOLLOW CATHODE LAMP

The lamp envelope (see Figure 1) consists of two compartments separated by a septum with a central hole (4 mm diameter). The cathode proper is a copper cylinder, with a diameter slot (4 mm wide, 10 mm deep), screwed onto the small-diameter extension of the polished, stainless-steel cone inserted in the rear of the cathode compartment. The gap between the copper cathode and the inter-compartment septum is just sufficient to accommodate the foil insert (0.1 mm thick). The insert of the metal to be analyzed is cut and shaped to cover the front face of the cathode and the interior surface of the slot.

A concealed O-ring seal has been used on the anode which necessitated fire-polishing the standard ground-glass cone, but it is acceptable to use vacuum grease to seal the joint between the cathode plug and the glass envelope since a continuous flow of argon (or neon) passes from the anode compartment to the cathode compartment via the cathode slot. This gas flow has two other useful effects: (1) it prevents deposition of the cathode metal on the silica window, and (2) it controls the composition of the plasma, thus preventing pulsing of the cathode discharge, at high operating currents, with ionizably difficult elements. Control of gas flow and pressure depends on the diameter of the capillary gas leak (see Figure 2) and the throttling action of the manostat working against the vacuum pumps (not shown).

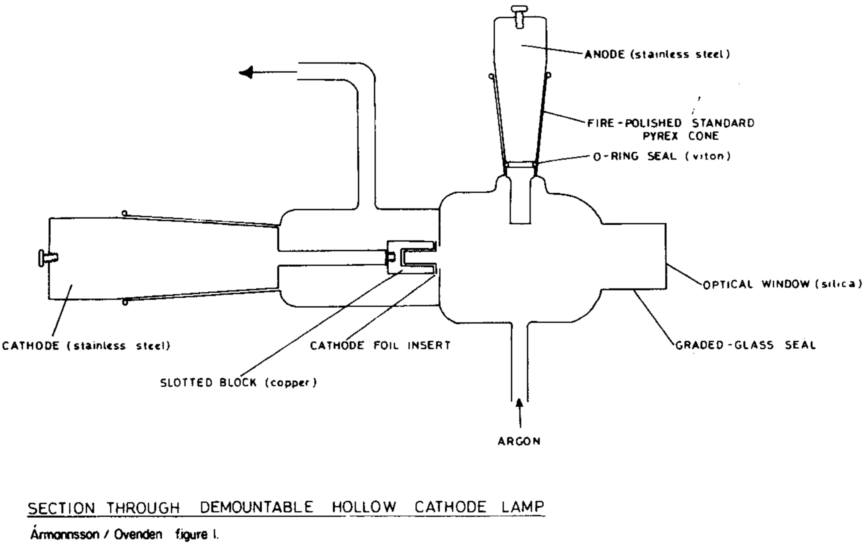

FIGURE 1 Section through demountable hollow cathode lamp.

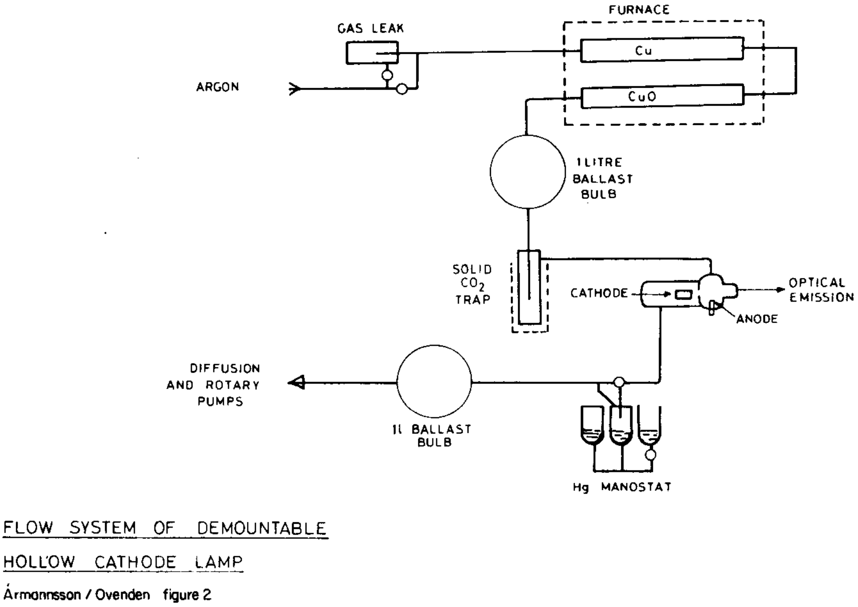

FIGURE 2 Flow system of demountable hollow cathode lamp.

Additional features are: (1) by-passes on the gas leak and manostat for rapid filling of the system with argon (neon) before changing the lamp foil and (2) the purification train (held at 400°C) trapping organic vapours from taps and flexible tubing upstream.

Concerning the preparation of hollow cathodes a procedure where a piece of copper foil was electroplated from a 4% (w/v) solution of bismuth in perchloric acid, proved satisfactory, but an analogous procedure for indium was unsuccessful since the indium was rapidly stripped off the copper foil when the lamp current was turned on. A successful alternative was to fill the diametric slot with solid indium and drill out a 4-mm hole. This procedure is recommended if ready-made foils of the metals in question are not available.

EXPERIMENTAL

Instrumentation

Varian Techtron Model AA5 atomic absorption spectrometer. Perkin–Elmer HGA-72 carbon furnace. Demountable hollow cathode lamp as described above.

Reagents

Use Analar reagents unless otherwise stated.

Dilute NH_3 solution. Add enough NH_3 to distilled water to make pH 8–9.

$CHCl_3$. Redistilled.

Dithizone solutions. Recrystallize by passing a current of filtered air into a nearly saturated solution of dithizone in $CHCl_3$ at 40°C, and wash the precipitate with a small amount of CCl_4. Make a 1000 ppm solution in $CHCl_3$ and purify by first shaking with alkaline water and then with 0.2 N HCl, using 1–200 ml of aqueous solution to each 100 ml of $CHCl_3$. From this solution prepare a 200 ppm solution in distilled $CHCl_3$ daily.

Constant boiling HCl. Conc. HCl and distilled water are mixed (8.25 ± 6.75) and the resulting solution distilled.

Procedure for silicate sediments

Weigh 1 g of sediment into a PTFE crucible (ca. 100 ml capacity), add 10 ml HF (Aristar grade), 5 ml H_2SO_4 (lead-free grade) and 0.5 ml $HClO_4$. Cover and leave on the sandbath at 100–150°C overnight. Remove the cover and leave open for 1 h. Transfer the contents to a 150-ml tall-form beaker. Heat the beaker on a hotplate until white fumes are given off.

Cool, add 0.5 ml $HClO_4$ and heat the mixture till dense fumes are evolved and most of the colour due to organic matter has disappeared; do not evaporate to (near) dryness. Cool, add water to make the volume 60–80 ml and heat on the hotplate until a clear solution is obtained. Cool, add 5 ml 50% (w/v) citric acid and ca. 10 ml NH_3 (Aristar grade). Cool again, transfer to a 100–150 ml separating funnel and adjust the pH to 8 with NH_3 or constant boiling HCl (indicator papers). Add 5 ml 1000 ppm dithizone, shake for 2 min and run the organic layer into a second 100–150-ml separating funnel. Raise the pH of the solution to 9.5 and repeat the extraction. Extract once more, this time with 5 ml 200 ppm dithizone. If the dithizone still changes colour, repreat the extractions until it does not. Wash the combined dithizone extracts with 5 ml dilute NH_3 solution. Run the dithizone layer into a third 100–150-ml separating funnel, wash the buffer solution with 5 ml $CHCl_3$ and add the washings to the dithizone extracts. Add 50 ml 0.2 N HCl to the dithizone extracts and shake vigorously for 1–2 min. Run the organic layer into a 150-ml tall-form beaker, wash the aqueous portion with 5 ml $CHCl_3$, add the washings to the dithizone solution and run the aqueous layer into the original 150-ml beaker.

Evaporate the aqueous solution to a 10–15-ml volume, add 0.5 ml $HClO_4$ and carry on the evaporation to dryness. Wash the sides of the beaker with ca. 10 ml distilled water, evaporate to dryness and take up the residue in 5 ml 2 N HCl (solution A).

Evaporate the organic extract to dryness, add 3 ml $HClO_4$, digest and evaporate to dryness on a hotplate. Repeat with 2 ml $HClO_4$. Wash the sides of the beaker with ca. 10 ml distilled water, evaporate to dryness and take up the residue in 5 ml 2 N HCl (solution B). Determine silver in solution B at 328.1 nm by flame a.s.s., other conditions being in accordance with the manufacturer's recommendations. Determine bismuth and indium by flameless a.a.s. as described below.

Procedure for calcium-rich sediments

Weigh 1 g of sediment into a PTFE crucible (ca. 100 ml capacity), add 20 ml constant-boiling HCl, and digest on the sandbath for 2–3 h. Transfer the contents to a centrifuge tube and spin. Add the supernate to a 150-ml tall-form beaker and evaporate slowly to dryness. Transfer the residue from the centrifuge tube back to the PTFE crucible, add 5 ml HF, 2 ml H_2SO_4 and 0.5 ml $HClO_4$, cover and leave on the sandbath at 100–150°C overnight. Remove the cover and leave open for 1 h. Add the contents to the 150-ml beaker containing the residue of the HCl extract. Heat the beaker on a hotplate until white fumes are given off, cool, add 0.5 ml

$HClO_4$, and heat the mixture till dense fumes are evolved and most of the colour arising from organic matter has disappeared. Add 50–60 ml of water and 20 ml constant-boiling HCl and heat. Add further 5 ml portions of HCl until a clear solution is obtained (total addition 30–40 ml), cool, add 10 ml 50% (w/v) citric acid solution, and 20–25 ml NH_3 (Aristar), and proceed as described above.

A.a.s. determination of bismuth and indium

Set the lamp at 233.1 nm for Bi and 303.9 nm for In and slit width 15 μm for Bi and 60 μm for In. Check the correct seating of the electrodes, evacuate the gas supply system to achieve a final pressure of ca. 1×10^{-4} Torr as a means of purging the purification train and as a check for leaks. Turn the furnace on and allow it to attain its working temperature of 400°C before admitting high purity argon (pressure 1 kg/cm^2) to the system. Turn the lamp power supply on (8 mA for Bi, 5 mA for In) and close the bypass to the manostat. Adjust the mercury level in the manostat to provide the optimum spectral output at the rated current. Provided the system is first filled with argon at atmospheric pressure a rapid change of cathode foil is possible without recourse to the full start-up procedure.

HGA furnace: Turn on a nitrogen gas flow (2 kg/cm^2, 1.5 N l/min) and cooling water. Adjust the control unit to the values shown in Table I.

Using a Perkin–Elmer, type 30062628 carbon tube introduce 100 μl of sample solution A; start the programme given in Table I. If bismuth is being determined, stop after the drying stage, introduce 100 μl of solution B; restart the programme and let it go to completion. Let the recorder chart run at minimum speed until just before atomization starts, but then speed it up to near maximum. Slow down again when the atomization

TABLE I

HGA-72 carbon atomizer programmes for bismuth and indium determinations

Control no.	Operation	Metal	Digital setting	Approximate temperature (°C)	Time (sec.)
1	Drying	Bi, In	016	90	300
2	Thermal destruction	Bi, In	050	400	90
3	Atomization	Bi	850	2250	15
		In	950	2270	15
4	Purge of carbon tube	Bi, In	990	2270	10

peak has appeared. Run blanks prepared in 2 N HCl in the same way as the solutions and standard solutions of the metals.

RESULTS AND DISCUSSION

Interferences with the bismuth determination could be kept at a minimum by using a freshly electroplated copper foil each time and was possibly due to Cu emission at 223.0 nm. The use of interrupted gas flow to increase sensitivity resulted in interference and is not recommended.

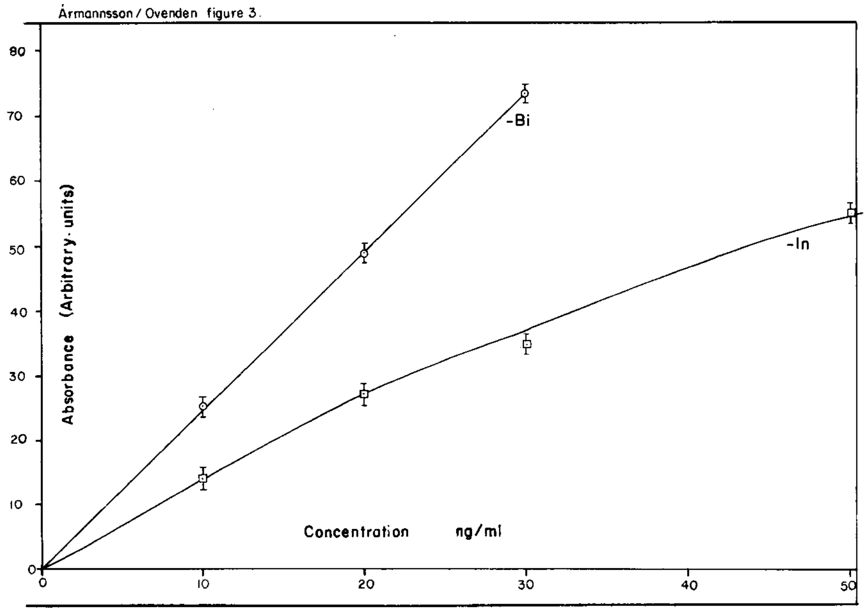

FIGURE 3 Calibration curves for bismuth and indium.

Standards containing up to 20–30 ng bismuth or indium per ml show approximately linear relationship between concentration and absorbance (Figure 3), but the curves tail off at higher concentrations. The coefficient of variation for repeated absorbance responses of a 20 ng/ml bismuth standard is 2.5 %. The detection limit is better than 1 ng/ml for bismuth, and about 1 ng/ml for indium.

A sediment sample from Fawley, Southampton Water, was spiked with silver, bismuth and indium and satisfactory recoveries were obtained (Table II). As the indium concentration in the sample itself was below the detection limit, a standard deviation could not be obtained from a replicate determination, but coefficients of variation for silver and bismuth, based on seven and four determinations respectively, are reported in Table II. Silver, bismuth and indium were also determined in three USGS rock reference samples. The indium values differed significantly from previously reported values,[5] but there was reasonable agreement for silver and bismuth (Table III).

TABLE II
The determination of silver, bismuth and indium in a sediment sample from Fawley, Southampton Water

Metal	Sample concentration (μg/g)	Spike (μg/g)	Spike recovery (%)	Coefficient of variation (%)	Detection limit (μg/g)
Ag	0.114	0.100; 0.200	100	26	0.03
Bi	0.281	0.060	111	7	0.01
In	<0.005	0.060	>95		0.01

TABLE III
Silver and bismuth concentrations found in three USGS rock reference samples

	Ag			Bi		
		Listed			Listed	
Sample	Found (μg/g)	Magnitude (μg/g)	Range (μg/g)	Found (μg/g)	Recommended value (μg/g)	Range (μg/g)
G-2	0.04	0.049	0.012–0.049	0.029	0.043	0.038–0.100
BCR-1	0.06	0.036	0.011–0.036	0.054	0.050	0.042–0.050[a]
AGV-1	0.09	0.11[b]	0.012–0.11	0.079	0.057	0.053–0.056[c]

[a] Excluding the high value 6 μg/g.
[b] Recommended value.
[c] Excluding the high value 5 μg/g.

Silver was determined in various sediments (Table IV). Generally the levels are of the same order as previously reported values.[3,6] High values at certain depths in cores from Fawley, Southampton Water, suggest local pollution, and patchy distribution in cores suggests that the silver is probably present in silver-rich particles and not evenly distributed throughout the sediment.

TABLE IV

Silver concentrations in various sediments

Location	Sample type	Mean Ag concentration (μg/g)	Range of Ag concentrations (μg/g)
Fawley, Southampton Water	Core samples	0.31	<0.05–1.22
Bristol Channel	Surface grab samples	0.23	0.05–0.67
Atlantic Ocean 20°48′ W, 18°01′ W	Core samples, brownish gray mud	0.15	0.05–0.34
Atlantic Ocean 20°48′ W, 22°41′ W	Core samples, red carbonaceous material	<0.05	<0.05–0.09

Analysis of dried powdered kale,[7] prepared as described in a previous paper[2] indicated that the bismuth and indium contents were below the detection limit (0.01 μg/g).

CONCLUSION

The application of a demountable hollow cathode lamp to trace metal analysis by a.a.s. shows promise. The lamp can be used satisfactorily for the determination of bismuth and indium and should be applicable to a.a.s. analysis of any element for which foils are commercially available.

Silver can be determined with adequate sensitivity by flame a.a.s. in solutions of most rocks and sediments, if the digestion/extraction technique described is employed, but bismuth must, in most cases, be determined by flameless a.a.s. Results obtained for indium in USGS reference rock samples were not satisfactory so the digestion/extraction technique in its present form cannot be recommended for this metal.

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