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Neutron Activation Determination of Mercury in Waters after Preconcentration by Flotation of Dithizone—Mercury Complexes

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Mercury in water samples, at levels below parts per billion, was collected by dithizone flotation. The statistical detection limit of Hg in seawater was 4 times better than that with a hydrous iron oxide—APDC flotation system in neutron activation determination. The same floated dithizone precipitate can be used repeatedly for collection from several volumes of the water sample. The Hg content in seawater was $0.017 \mu\text{g/L}$. Average recovery from waters containing $0.025 \mu\text{g/L}$, $0.05 \mu\text{g/L}$ and $0.1 \mu\text{g/L}$ was 98%. The method was applied successfully to the determination of Hg in NBS 1641b. Methyl mercury is also collected by the procedure described.

KEY WORDS: Neutron activation-mercury-dithizone, mercury determination, dithizone flotation, water samples.

INTRODUCTION

Considerable development in the analytical methodology of mercury has occurred since the tragedy of Minimata and the discovery that the cause was the high level of mercury in fish.¹ We now know that mercury is everywhere and monitoring of its level is a necessary and common practice. The mercury content in natural water samples is often too low to be determined directly, even by the most sensitive

techniques, and preconcentration is therefore required. This has been achieved by amalgamation of mercury vapour released from water samples with reducing agent prior to a.a.s. determination.²⁻⁴ It is difficult, however, to so treat the large volume of water required for low mercury concentration and some work has been done in developing preconcentration with absorptive resins,⁵⁻⁷ cellulose,^{8,9} columns packed with Wakogel-200¹⁰ and polyurethane foams.¹¹ These methods are often time consuming due to adsorption-elution requirements, low flow rate and the need to refilter several times for complete collection. Adsorption colloid flotation avoids these difficulties; it permits rapid and simple preconcentration of traces from large solution volumes. It has additional merit when neutron activation (or X-ray fluorescence) is used for measurement because direct analysis of the collected elements is possible.

Both cations and anions in water samples have been preconcentrated by flotation of hydrous iron oxide—APDC and determined by neutron activation.¹² Complete recovery of mercury was also obtained from spiked samples but it was not possible to detect low mercury levels because of background from adsorbed sodium ions and from iron. Organic co-precipitants are advantageous for determination of elements by neutron activation but not all organic precipitants will float; dithizone, however, can be floated easily¹³ when fine nitrogen gas bubbles are used and it binds strongly and selectively with mercury. The determination of mercury at less than $0.1 \mu\text{g/L}$ level in water samples by n.a.a., after preconcentration by flotation of dithizone-mercury precipitate, is described in this paper.

EXPERIMENTAL

Apparatus

All samples were irradiated in the Dalhousie University SLOW-POKE reactor at a flux of $5 \times 10^{11} \text{ n.cm}^{-2} \cdot \text{s}^{-1}$. The activated samples were then counted at 77 keV in a Low Energy Photon Detector (LEPD—Aptec), resolution 0.560 keV, connected to a Jupiter Multi-channel Analyser (Canberra).

The flotation apparatus was as described previously.¹⁴ However a 2 L beaker, with a tap near the bottom, was used for flotation to permit treatment of large volumes of water. A Nuclepore membrane

filter (0.40 μm pore size, 47 mm diameter) was utilized to collect floated precipitate rather than a Gelman Metrical membrane filter because the dithizone precipitate was more easily removed from it.

Chemicals

The dithizone available usually contains mercury and must be purified. It was found that the most simple and effective way to purify dithizone was to extract it with chloroform from a solution containing 2% KI at pH 5–6. Three grams of dithizone were dissolved in 200 ml of 25% (V/V) ammonia and ultrex nitric acid (50% V/V) added to 100 ml of the filtered solution to a pH 5 to 6. Two grams of potassium iodide were added and the solution containing the precipitated dithizone was shaken with 100 ml of chloroform. The organic phase, after being washed four times with 100 ml aliquots of deionized–distilled water, was then evaporated at room temperature and the purified dithizone stored in a dark bottle.

A standard solution (100 $\mu\text{g}/\text{ml}$) of mercury was prepared by dissolving mercuric chloride (A.C.S.) in deionized–distilled water.

Natural seawater from the Northwest Arm, Halifax, Nova Scotia was collected directly from the taps in an Oceanography laboratory of the university; the water is filtered through a sand bed before entering the building.

Sample treatment

Two liters of water samples, acidified to pH 3–4 with Ultrex nitric acid (50% V/V), were taken for analysis. Purified dithizone (50–100 mg) dissolved in 10 ml of dioxane was added dropwise with stirring and, after 15 minutes, nitrogen gas was bubbled through the stirred solution; the gas was passed through a porosity F frit at a flow rate so that bubbles just broke the surface of the solution. The clear solution with the floated dithizone precipitate on the surface was then drained through the tap with the nitrogen gas bubbling through the solution continuously. Additional 2 liter aliquots of acidified water sample were added to the beaker with stirring. Ten mL of dioxane was then added and the flotation process (without addition of further dithizone) was repeated.

The floated dithizone was transferred to the membrane filter immediately after stirring was stopped. The collected precipitate was washed with deionized-distilled water several times and dried with filter paper. It was then carefully removed and transferred into a polyethylene bag which was irradiated after sealing. The blank was obtained by collection of the same amount of dithizone from deionized-distilled water according to above procedure. The standards were prepared by adding known concentrations of standard solution to the blank precipitate of dithizone.

Artificial fresh water samples were prepared either by adding known concentrations of mercury (or methyl-mercury) to deionized-distilled water or by dilution of the NBS 1641b sample.

After irradiation for 16 hours, the activated samples were allowed to decay for 3 days prior to γ -ray measurement at 77 keV. For samples containing more than 0.1 μg , 30 min of counting time was sufficient, but several hours counting is recommended for samples containing less than 0.1 μg Hg; blank samples should be counted, of course, for the same time period as the measured samples.

RESULTS AND DISCUSSION

Flotation and collection

The flotation of dithizone can be done easily and quickly without any surfactant over a pH of 1 to 5 if fine bubbles of nitrogen are passed through the stirred solution. It is, however, worth noting that miscible solvents used for dissolving dithizone, such as 1,4-dioxane and acetone, do play an important role in generating numerous tiny bubbles as well. In fact, flotation and collection of the dithizone precipitate was not complete if a miscible solvent was not present; 1,4-dioxane is recommended because it was more effective than acetone. Delay in transfer of floated precipitate results in losses due to adherence of the precipitate to the beaker wall and transfer tubing. Mercury(II) was quantitatively collected over a pH range of 1 to 4. Although collection decreased at pH 4-5, more than 90% recovery was still obtained. The quantitative collection of Hg(II) over such a wide pH's range is of value if collection of other elements, such as Cd(II), is desired. Figure 1 shows that both Hg(II)

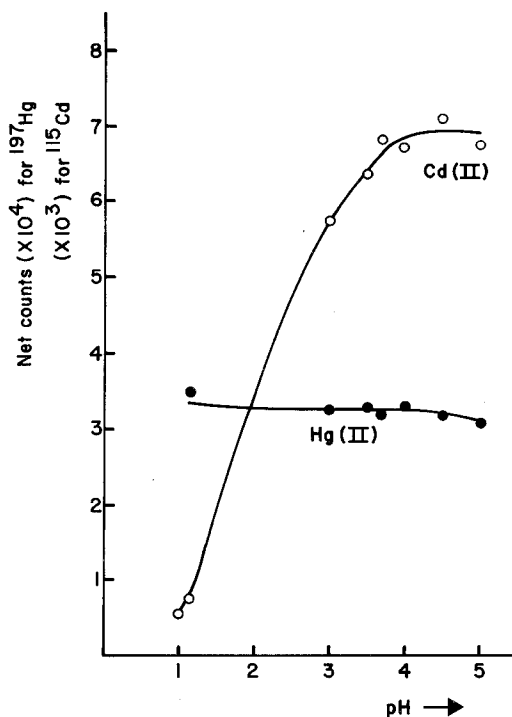


FIGURE 1 Effect of pH changes on collection of Hg(II) and Cd(II) .

and Cd(II) can be collected quantitatively at $\text{pH } 3.5 \sim 4.5$ with flotation of dithizone. Collection of toxic Cd(II) by this procedure has merit in samples which have a complex matrix, such as seawater, even though the sensitivity for cadmium using a low flux reactor is not good enough for quantitative determination by n.a.a. The collected dithizone precipitate is easily dissolved for determination of cadmium by other techniques.

The recovery of mercury is dependent on the solution temperature and the stirring time. Quantitative recovery was obtained up to 40°C but decreased with increased temperature (64% at 54°C , 15 min stirring). At room temperature, recovery was complete for stirring times in excess of 10 min; 78% recovery was observed for 5 min stirring. Flotation, therefore, should be done at room temperature, with stirring for 15 min.

Detection limit

The statistical detection limit based on $2(\text{background})^{1/2}$ is $0.01 \mu\text{g}$ and $0.017 \mu\text{g}$ of Hg for fresh water and seawater respectively. Much lower detection limits ($0.002 \mu\text{g}$ of Hg) can be obtained by counting for 12 hours.

The blank results mainly from the dithizone available (Table I). For purification of dithizone, several approaches were taken. The data in Table I show that it is most effective to extract dithizone reprecipitated in aqueous solution, with chloroform in the presence of 2% KI (W/V) at pH 5–6. Although $0.02 \mu\text{g}$ of Hg per 100 mg of dithizone was still present, the blank for purified dithizone is more than 10 times lower than that of unpurified. The detection limit, based on $2 \times$ standard deviation of blank determinations, was $0.01 \mu\text{g}$. It is therefore possible to determine very low levels of Hg in water samples, if a large volume of water sample is preconcentrated, without increasing the reagent blank.

TABLE I
Blank and purification of dithizone

	Media from which dithizone was extracted	Blank of Hg in dithizone, $\mu\text{g}/100 \text{ mg}$	Ref. procedure
Unpurified	—	0.27	
Purified	6N hydrochloric acid	0.19	15
	6% NH_4I at pH 4	0.16	16
	2% KI in 0.1 M HCl	0.12	16
	2% KI at pH 5–6	0.02	this work

Preconcentration of Hg from large volumes of water and determination of Hg in seawater

The floated dithizone precipitate still has good ability to collect mercury(II) and this makes it possible to reuse the floated dithizone precipitate for collection from several volumes of water sample without increasing the amount of dithizone used. As a result, the reagent blank is maintained at a low level, while mercury continues to be concentrated. Table II shows that recoveries of 0.025, 0.05 and $0.1 \mu\text{g}/\text{L}$ of Hg(II) were quantitative with floated dithizone pre-

TABLE II
Recoveries and content of Hg in water samples

Water samples	Hg, $\mu\text{g/L}$			Ref. or certified value of Hg, $\mu\text{g/L}$	
	Species added	Found	Recovery %		
Deionized-distilled water	Hg(II)	0.025	0.024	95	—
		0.050	0.054	108	—
		0.100	0.095	95 ± 9^a	—
	CH ₃ Hg(I)	0.100	0.110	110	—
NBS 1641b	—	1.52 ± 0.05^a		1.52^b	
Seawater	—	0.017 ± 0.002^c		0.020^8	

^aQuadruplicate results.

^bThe value of Hg NBS 1641b should have after 1000-fold dilution.

^cDuplicate results.

precipitate repeatedly used for collection from several volumes of sample.

The relative standard deviation for $0.1 \mu\text{g/L}$ of Hg was 9% which is reasonable in practical determination.

The mercury in seawater was preconcentrated from 8 L samples with 100 mg of dithizone. The content of Hg in seawater was determined to be $0.017 \mu\text{g/L}$ which agrees well with results obtained previously.⁸

As an artificial fresh water standard, NBS 1641b was diluted 1000 times and then analyzed; results in Table II show the excellent agreement with certified value.

It is worthwhile to note that the recovery of methyl mercury added to deionized-distilled water was quantitative as well and both inorganic mercury(II) and methyl mercury are collected by the procedure described.

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