

# Lead Sulphide as a Sorbent for the Preconcentration of Mercury from Air and Determination of Mercury by Atomic Emission Spectroscopy\*

S. Alexandrov

Chair of Analytical Chemistry, Faculty of Chemistry, University of Sofia, A. Ivanov 1, BG-1126 Sofia, Bulgaria

## Bleisulfid als Sorbent für die Anreicherung von Quecksilber aus Luft und Bestimmung von Quecksilber mittels Atomemissionsspektrographie

**Zusammenfassung.** Bleisulfid, synthetisiert durch Fällungsreaktion zwischen wässrigen Lösungen von Bleiacetat und Natriumsulfid (pH 1), erwies sich als sehr wirksames Adsorptionsmittel für Quecksilberdampf aus Luft. Der Kollektor, der eine bestimmte Menge Quecksilber aus einem bekannten Volumen absorbiert hat, wird in eine Eisenhohlelektrode eingebracht und das Quecksilber durch Emissionsspektrographie (Gleichstrombogen, fotografische Registrierung der Spektren) von Proben und Standards bestimmt. Die Nachweisgrenze liegt bei ungefähr 0,1 µg und die relative Standardabweichung beträgt 9% bei 1 µg Quecksilber.

**Summary.** Lead sulphide, if prepared by precipitation reaction between lead acetate and sodium sulphide, both in aqueous solution, and adjusted to pH 1, has been shown to be an efficient absorbent for mercury vapour from air. After a portion has been used to collect mercury from a measured volume of air, it is packed into a hollow iron electrode and the mercury is determined by emission spectrography with a dc arc and photographic recording of the spectra from samples and standards. The limit of detection is about 0.1 µg, and the relative standard deviation 9% at the 1 µg level.

## Introduction

The determination of mercury in environmental samples is important for reasons of industrial hygiene, and has been reviewed by a number of authors [1–3]. Because of the low levels of mercury in air and its high toxicity, preconcentration is necessary. A wide variety of absorbants, liquid and solid, have been proposed. They include as solutions in water, potassium iodide plus iodine, sulphuric acid plus potassium permanganate and sodium hypobromite. The following have been employed as solids: activated charcoal, either alone or modified by treatment with hydrochloric, nitric or sulphuric acids, alkaline sulphides or polysulphides etc., noble metals such as gold, rhodium and palladium, silica gel soaked in aqueous potassium iodide, anhydrous

magnesium sulphate dipped in a solution of potassium iodide and iodine, silver oxide, manganese dioxide, and a mixture of sulphur and selenium.

This paper presents the results of a study of the possibility of combining adsorption of mercury vapour from air onto lead sulphide with an emission spectrographic determination. Lead sulphide has been shown to be an efficient collector for mercury in solution; it can be added as such to an aqueous sample, or prepared in situ by simultaneous addition of solutions of sodium sulphide and lead acetate to the sample solution [4–9]. Subsequent determination of the mercury may be performed by neutron activation analysis or emission spectrography. Lead sulphide has not previously been used to collect mercury vapour from air.

## Experimental

**Reagents.** Lead sulphide was purchased from VEB Laborchemie, Apolda, or was synthesized in our laboratory by mixing solutions of sodium sulphide and of lead acetate at pH 1, with either one or the other reagent in excess (in different experiments), decanting the supernatant liquor and drying the precipitate at 105–110°C. An X-ray diffraction pattern showed the product to have the same crystal structure as natural galena, PbS.

Radioactive  $^{203}\text{Hg}$  tracer was obtained by neutron activation of mercuric oxide in a reactor and subsequent dissolution in nitric acid. (The half-life of this isotope is 47 days.) A standard solution of 1 mg/ml of mercury from Hopkin and Williams was used to prepare dilute aqueous solutions.

**Apparatus.** Known amounts of mercury vapour in air were produced by adding 3 ml of tin(II) chloride solution (10 g of the hydrated salt dissolved in 20 ml of concentrated hydrochloric acid, filtered and diluted to 100 ml with water) to 1 µg of mercury (added as a dilute standard solution) in a closed vessel which could then be swept out with air or some other carrier gas to transfer the mercury vapour to the adsorption tube. The apparatus is shown in Fig. 1. In some experiments where a larger amount of mercury was required, the air from a closed vessel over the surface of some liquid mercury was used instead. This offers convenience, but the concentration of mercury in the air is of course too high.

The sorption behaviour of lead sulphide was investigated by packing it into a glass tube with an internal diameter of 3 mm such as is shown in Fig. 2a. The effect of changes of temperature was examined by using the water-jacketed tube

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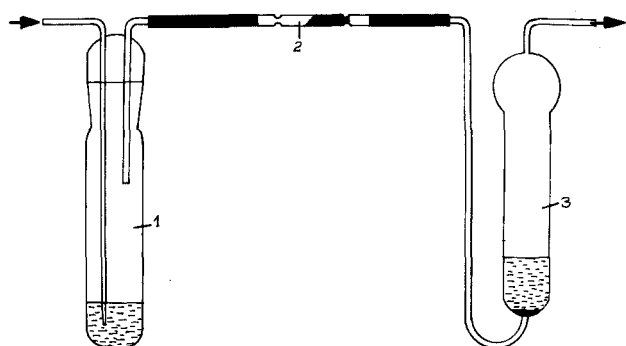


Fig. 1. Apparatus used for producing mercury vapour and collect it on lead sulphide sorbent. 1 Vessel for producing mercury vapour; 2 sorption tube; 3 adsorption tube with KI/I<sub>2</sub> for checking recovery

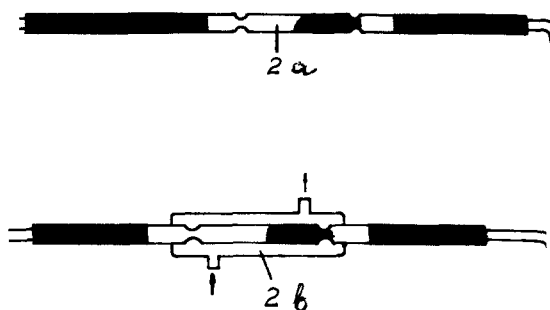


Fig. 2. Adsorption tubes for use with lead sulphide. *a* Simple tube for routine use; *b* water-jacketed tube for investigating the effect of temperature

shown in Fig. 2b. Each experiment was carried out with a 0.2–0.4 g portion of lead sulphide packed into the tube.

Hollow iron electrodes (Fig. 3) were packed with the entire portion of lead sulphide from the glass tube after collection of mercury and were excited in a dc arc with about 10 A [7–9]. The emission spectra obtained with a PGS-2 spectrograph with a grating of 650 lines/mm and a slit-width of 0.025 mm, were recorded on ORWO type WU-2 plates exposed for 100 s. Standard developer (time 4 min 30 s) and fixer were used. The optical densities were measured with a microphotometer type D-II. Volumes of air passed through the absorption tubes were determined from flow rates measured with a rotameter.

**Procedure.** Volumes of standard mercury solution containing 0.2, 0.5 and 1.0  $\mu\text{g}$  were added to portions of lead sulphide weighing 0.2–0.4 g. These were dried at 60–80°C, packed into iron electrodes and the emission spectra recorded. Each amount of mercury should be taken in duplicate. Finally, the spectrum for the sample is recorded on the same plate, the plate developed and the line intensities measured. The amount of mercury is estimated from the calibration curve. A typical curve is shown in Fig. 4. The curvature at the lower end of the graph is typical for this type of plate and is due to the sensitivity of the emulsion.

## Results and Discussion

The collecting efficiency of lead sulphide for mercury was investigated using the <sup>203</sup>Hg radiotracer and appropriate

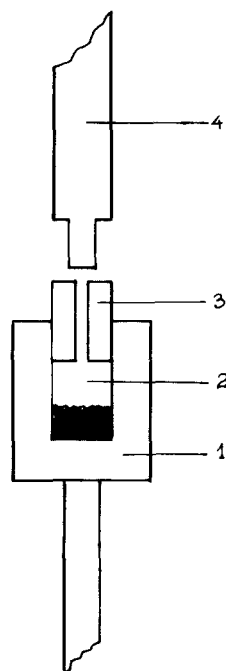


Fig. 3. Hollow iron electrode. 1 Electrode body; 2 electrode chamber; 3 carbon electrode fitted to hold in place the lead sulphide; 4 carbon counter electrode

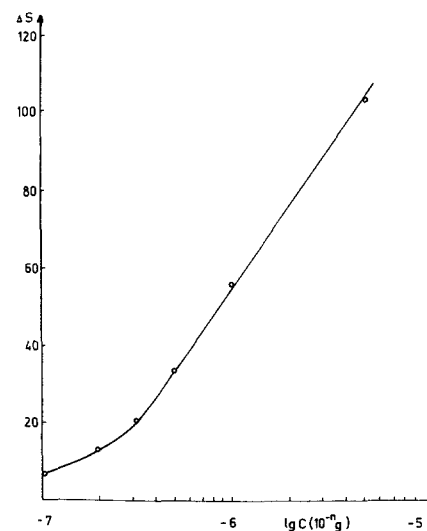


Fig. 4. Typical calibration curve

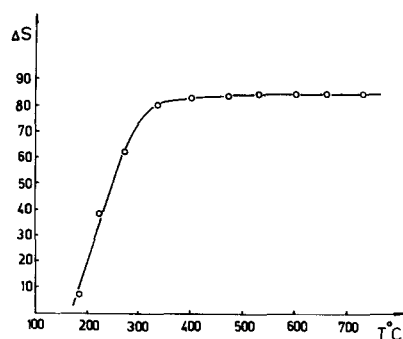


Fig. 5. Loss of mercury from lead sulphide collector after heating for 10 min at different temperatures

**Table 1.** Mercury levels in the air of some laboratories

Laboratory	Mercury level, $\mu\text{g}/\text{m}^3$	
	New method	Atomic absorption
Qualitative analysis lab	0.2	0.1
Quantitative laboratory	0.4	0.4
Instrumental laboratory	0.5	0.6
Dental surgery	0.4	0.5

counting equipment, taking care to keep the same counting geometries for all samples, and also by using the emission spectrographic method.

The method of preparation of the lead sulphide is important: if prepared with an excess of sodium sulphide its adsorptive powers are very good. Recoveries of mercury were such that the air passed through a tube did not have sufficient mercury to be detected by the methods used, either chemically or radiochemically. Further, passage of air through a tube which had already been used to collect some mercury showed no loss of mercury after 48 h. Experiments using larger amounts of mercury showed that 100  $\mu\text{g}$  could be collected with no loss, but 1 mg exceeded the capacity of the 0.2–0.4 g portions of lead sulphide.

Though the generation of mercury vapour is not a part of the proposed method, the efficiency of this step was also checked using the  $^{203}\text{Hg}$  tracer and found to be always better than 95%. Temperature does not affect the adsorption efficiency in the range of 20–100°C, suggesting that the process depends on chemisorption rather than simple adsorption. Higher temperature will bring about release of the mercury, as can be seen from the results in Fig. 5. Air or nitrogen may be used as carrier gas for the adsorption experiments without affecting the results. Possible interference from other vapours must be taken into consideration, as factory or laboratory atmosphere could well contain other species besides mercury. Ammonia, carbon dioxide,

carbon monoxide, and vapours of concentrated hydrochloric, sulphuric and nitric acids did not affect the adsorption efficiency.

*Performance of the Method.* Reproducibility of the method at the 1  $\mu\text{g}$  level was checked by analysing 10 samples in succession. The relative standard deviation was 9%. Repeated measurements on the background of the plates at the 253.6 nm line indicated that the limit of detection was around 0.1  $\mu\text{g}$  of mercury, equivalent to Kaiser's value of three times the standard deviation on the blank.

As comparison, similar amounts of mercury were collected in sulphuric acid/permanganate solution, reduced by hydroxylamine hydrochloride and determined by the cold-vapour atomic absorption method [10].

*Application of the Method.* Both the proposed spectrographic and the atomic absorption methods were used to determine mercury vapour levels in some laboratories. The average values from five determinations by each method in each laboratory are shown in Table 1. The agreement between the sets of results is satisfactory, and the method can be recommended for use in laboratories which already have emission spectrography in routine use.

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