

Environmental Mercury: Rapid Determination in Water at Nanogram Levels

Abstract. Mercury compounds and free mercury are determined by emission spectrophotometry in a radiofrequency helium plasma. The method is simple, rapid, directly applicable to environmental water samples, and subject to few interferences. The useful working range is 10 nanograms to 10 micrograms, or 1 part per billion to 1 part per million in 10 milliliters of sample. The limit of detection is about 2 nanograms.

The recognition of mercury pollution as a serious environmental problem has emphasized the need for a rapid analytical method capable of measuring trace amounts in natural water systems. Conventional colorimetric, atomic absorption, and flame emission techniques lack the necessary sensitivity, and the only method previously useful for routine measurements at the parts per billion (ppb) concentration level was atomic absorption with the use of large samples and either a cumbersome preconcentration or volatilization coupled with long-path absorption. We have found that plasma emission spectroscopy provides a rapid and simple means of measuring nanogram to microgram amounts in small samples.

The technique is basically that of flame photometry with the flame replaced by a radiofrequency plasma in helium at atmospheric pressure. The high emission sensitivity of mercury in the helium plasma and an extremely

efficient system for extracting the mercury from the sample in a small volume of helium gives the method its striking advantages. The effective sensitivity is over 1000-fold greater than that of conventional hydrogen-oxygen flame emission. The sample, 10 ml of water or aqueous solution, is placed in the sample cell *A*, a 30-ml, coarse-grade, fritted-glass filtering funnel (Fig. 1). A slight pressure of helium is maintained at *I* to keep the sample from leaking through. Simultaneously, a flow of helium (1 liter/min) saturated with water vapor by passing through a gas washing bottle with a fritted-glass bubbler is maintained through the bypass *B* into the plasma torch chamber and up the quartz chimney *Q*, past the torch tip *T*. The emission from the plasma *P* is monitored at 2537 Å by means of a monochromator-photomultiplier detection system of conventional design. The helium flow is diverted from the bypass to the bottom of the sample cell so that it bubbles through the sample before passing to the torch chamber. When the base line is stable (30 to 60 seconds) 0.5 ml of 2 percent titanous chloride in 1M sulfuric acid is added by syringe through the serum cap *S*. The resulting very rapid reduction of mercury compounds to the elemental state and purging of the mercury vapor by the helium stream causes a rise in emission intensity starting in about 10 seconds and reaching a maximum in about 20 seconds (Fig. 2). Peak height is proportional to the total amount of mercury in the sample, and the stripping is usually complete in 2 minutes. The flow is then returned to the bypass, the sample discarded, and the cell rinsed, whereupon the next sample may be introduced immediately.

A typical response for 10 ml of 30 ppb mercurous nitrate is shown in Fig. 2, curve 1. The small peak obtained after starting the helium sparging at *A* is a measure of the free metallic mercury in the sample resulting from the presence of a reducing agent or simply

from the disproportionation equilibrium of mercurous ions to give mercuric ions and elemental mercury. Addition of a small concentration of an oxidizing agent, such as dichromate ion, to the sample before sparging eliminates this peak. It is evident that the method will distinguish and determine both combined and elemental mercury in the same sample. The addition of 100 μ l of 100 ppb mercurous nitrate (10 ng of mercury) to a blank consisting of 10 ml of deionized water and 0.5 ml of titanous reagent in the cell resulted in a curve (Fig. 2, curve 2) that suggests that 2 ng is the limit of detection with our present apparatus. The quantitative working range is approximately linear for concentrations from 1 to at least 1000 ppb.

No interferences have been observed in the emission process itself, but the presence of some substances may hinder the release of mercury from the sample mixture. Noble metal compounds may be reduced to the metals by the titanous reagent and thus retain mercury. Silver, palladium, and gold caused interference when present in 100-fold greater concentration than mercury, but the likelihood of such concentrations being found in natural water samples is small. Lead, cadmium, zinc, and copper showed no effect in 1000-fold excess. Chloride in concentrations over 0.1M caused a slight de-

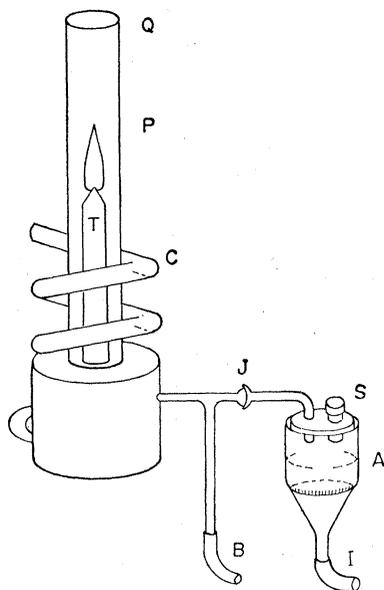


Fig. 1. Sample and excitation chambers. Symbols are: *A*, sample cell; *B*, inlet for bypass helium; *C*, torch RF coil; *I*, inlet for stripping helium; *J*, ball joint connector; *P*, plasma discharge; *Q*, quartz chimney; *S*, serum cap; and *T*, torch tip.

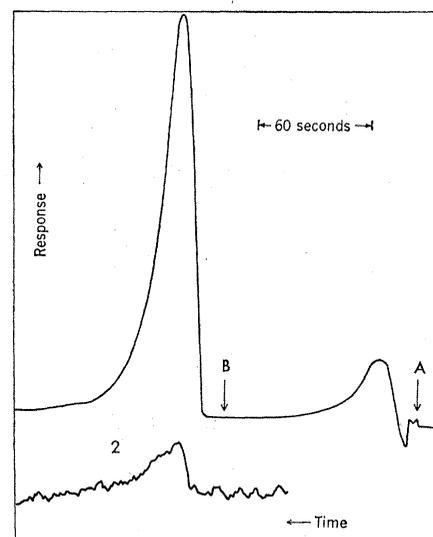


Fig. 2. Typical response curves. Curve 1 shows the response of 10 ml of 30 ppb mercurous nitrate (see text). At *A*, the helium flow was started; at *B*, the titanous reagent was injected. Curve 2 shows the effect of the addition of 10 ng of mercury (see text).

pression. Such effects may be compensated for by adding comparable amounts of the interfering component to the standards, or by injecting a known amount of mercury solution into the sample after the recorder has returned to the base line (standard addition technique). Phenyl mercuric chloride and methyl mercuric bromide behaved the same as inorganic mercury salts. Dimethyl mercury, however, was indistinguishable from elemental mercury, because it was completely purged from the sample before the addition of titanous reagent. Presumably other highly volatile mercury compounds behave similarly. No difficulty was encountered in applying the method to natural water samples. Water from the Charles River (a stream polluted with raw sewage) showed no detectable mercury, but quantitative recovery of added mercury was attained at the 5 ppb level, both immediately and after 24 hours. Similar results were obtained with seawater.

All the equipment used other than the plasma torch unit is commercially

available. The unit itself is of simple design and may be constructed for \$500 to \$1000 including labor. Our instrument is the one described by Hume and West (1), which was slightly modified for this application. The principal changes are an aluminum torch tip, a quartz chimney (22 mm, inner diameter) to reduce dead volume, the sample handling system described above, and the elimination of the capacitive link to ground. The unit has been in use for several years and requires only minimum maintenance. The replaceable torch tip has a life of a few hundred hours and a tank of helium lasts from 75 to 100 hours.

ROBERT W. APRIL

DAVID N. HUME

Department of Chemistry,
Massachusetts Institute of Technology,
Cambridge 02139

References and Notes

1. C. D. West and D. N. Hume, *Anal. Chem.* **36**, 412 (1964).
2. Supported in part by AEC contract AT(30-1)-905.

19 August 1970

A High-Pressure Polymorph of Troilite, FeS

Abstract. A new polymorph of FeS was produced in a diamond-anvil cell and observed at high pressure both optically and by x-ray diffraction. Fourteen x-ray reflections of the high-pressure FeS were recorded; however, the crystal structure is unknown. This form of FeS is stable at 25°C only at pressures above approximately 55 kilobars. The transition to the lower pressure polymorph, troilite, is rapid and reversible.

Troilite, the end member of the pyrrhotite solid solution series, is stoichiometric FeS. This mineral is common in certain terrestrial deposits and most

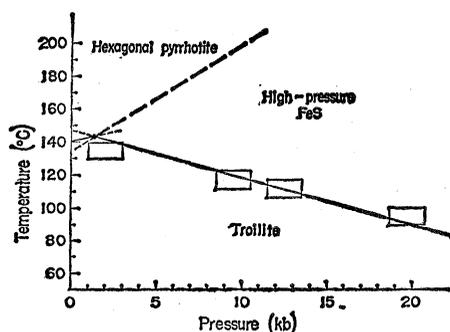


Fig. 1. Pressure-temperature diagram of FeS. The curve between the high-pressure FeS and troilite fields associated with the data of Kullerud *et al.* (2) is consistent with their data, that is the rectangles, but is slightly different from their original curve. This modification was made in order to draw in the schematic phase relations.

meteorites, and is ubiquitous to all lunar samples from the Apollo 11 and 12 missions. Many of the rocks containing troilite have been exposed to high pressure either during or subsequent to their formation (for example, shock features of lunar samples) and it is thus important to establish the stability region of troilite in pressure-temperature space.

Troilite is the polymorph of FeS stable below the α transition that occurs at 140°C and approximately 1 atm pressure. This polymorph has a supercell based on the NiAs-type (B-8) structure. Above 140°C, hexagonal pyrrhotite, with the simple hexagonal B-8 structure or some minor supercell modification thereof (1), is the stable phase at low pressures.

Kullerud *et al.* (2) determined by differential thermal analysis the effect of pressure on this α transition from about 2 to 19.7 kb and found that pressure lowers the transition temperature

by about 2.2°C/kb, indicating a negative ΔV for the transition from low to high temperature. Taylor (1), on the basis of a high-temperature x-ray diffraction study resulting in a plot of cell volume versus temperature, reported a ΔV associated with the α transition of $\approx +0.22 \text{ \AA}^3/\text{mole-FeS}$. He calculated the effect of pressure on the transition, with the value for ΔH from Robie and Waldbaum (3), to be +2.3°C/kb, that is, increased pressure should raise the transition temperature. Taylor (1) suggested that this apparent discrepancy could be explained by the presence of a high-pressure polymorph of FeS with an approximate arrangement of univariant curves as shown in Fig. 1.

The FeS was synthesized from the elements, of 99.99+ percent purity (by weight), in sealed, evacuated silica-glass tubes annealed at 700°C for 2 days, followed by quenching, grinding, and re-sealing in a new silica tube with additional annealing for 14 days. The d_{102} value of this material at 22°C was $2.0932 \pm 0.0009 \text{ \AA}$, identical with the value commonly accepted for FeS (4). Optical examination of this starting material in polished section did not reveal the presence of Fe or any other phase besides troilite. This polycrystalline FeS sample was compressed in a diamond-anvil, high-pressure cell (5) and x-rayed at pressure with the use of $K\alpha$ radiation from an Mo source and exposure times of approximately 14 days. The pressure within the cell was previously calibrated against the force applied; various standards were used. Experiments at $120 \pm 40 \text{ kb}$ and 22°C, and $50 \pm 20 \text{ kb}$ and $120^\circ \pm 30^\circ\text{C}$ revealed the presence of a new high-pressure form of

Table 1. The x-ray diffraction data for high-pressure FeS.

120 \pm 40 kb, 22°C		50 \pm 20 kb, 120° \pm 30°C	
<i>d</i> (\AA)*	<i>I</i> †	<i>d</i> (\AA)*	<i>I</i> †
3.645	1		
3.236	1	3.366	1
2.843	10	2.869	10
2.582	6	2.617	4
2.444	6	2.475	4
2.250	2	2.278	2
2.113	6	2.155	3
1.979	10	2.015	5
1.881	4	1.909	1
		1.845	1
1.754	5	1.770	5
1.632	6	1.644	9
1.502	3		
1.412	2	1.425	3

* The estimated error in the *d* values is 0.5 percent. † Some preferred orientation was present in this sample at pressure, evidenced by the non-uniform density of the reflections as recorded on the film.