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ATOMIC ABSORPTION AND EMISSION SPECTROMETRY
OF MERCURY AT 184.9nm.

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We have previously described qualitative measurements concerning the feasibility of atomic absorption spectrometry of mercury at 184.9nm (1). This communication describes the analytical utility of such measurements together with some atomic emission studies using a conventional monochromator system purged with an inert gas to prevent absorption of radiation by oxygen.

Experimental

(a) Atomic Absorption Studies.

The primary source of resonance radiation was a mercury microwave excited electrodeless discharge lamp (some 10cm long), operated at ca 15 watts in a foreshortened 3/4 wave resonant cavity (Electro-Medical Supplies Ltd.). The line intensity at 184.9nm and stability were increased by cooling the lamp; argon was used for this purpose at a flow rate of 1.8 l min^{-1} .

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The experimental arrangement is shown in Fig. 1. Radiation from the lamp (A) was passed through the absorption tube (C) (length 11 cm, internal diameter 2 cm) via a slit (B) (width 2mm), before entering the grating monochromator (D) (Rank Precision Industries Ltd., Type D330 with a linear dispersion of $26 \text{ \AA/mm}^{\circ}$). The monochromator was flushed with argon ($\text{ca. } 3 \text{ l min}^{-1}$) to remove atmospheric oxygen which absorbs strongly at wavelengths below 200 nm. (Nitrogen could also have been used with similar results).

The photomultiplier (G) (EMI Ltd., Type 6256 S) output was measured on a Servoscribe potentiometric chart recorder with a 20 μF capacitor across the input terminals to reduce short term noise.

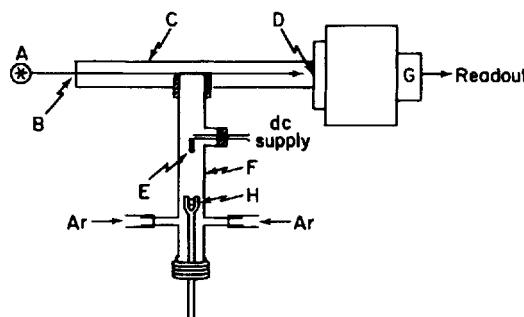


Figure 1. Schematic representation of atomic absorption system.

- A - Hg discharge lamp
- B - Slit
- C - Absorption tube
- D - Slit
- E - Pt loop
- F - Glass sleeve
- G - Monochromator and photomultiplier
- H - Sample cup

A platinum loop sampling and nebulising device (2) was used to introduce the sample into the absorption tube (C); This was achieved by raising the sample cup (H) containing the test solution so that the platinum loop (E) dipped into it and picked up a surface tension film of ca 0.1 μ l. The water was evaporated by passing a small dc current through the loop (Fig. 2); the dried sample was then atomised by passing a sufficient dc current to heat the loop rapidly to just below its melting point (ca 1,500°K). Argon was used as the carrier gas.

(b) Atomic Emission Studies

The experimental system was similar to that used for the atomic absorption studies except that no source of radiation was used and the platinum loop sampler terminated in a short length (ca. 4cm) of narrow bore (2mm) quartz tubing. Within this section of tubing an atmospheric argon plasma was initiated (flow rate 1.8 ml/min) using a $\frac{1}{4}$ wave resonant cavity coupled to a microwave generator operating at a power of ca 40

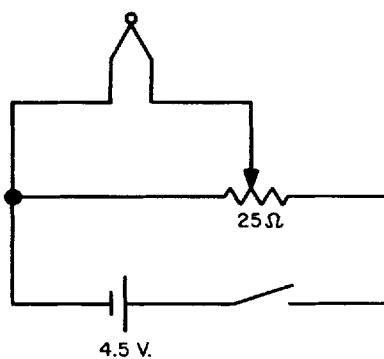


Figure 2. Electrical circuit for heating the Pt loop.

watts (2). The monochromator slit widths were set at 0.05mm and the plasma was adjusted such that it filled the monochromator entrance slit.

RESULTS AND DISCUSSION

Atomic absorption measurements were made at 253.7nm (intercombination line) and 184.9nm (resonance line) using solutions prepared from mercuric chloride.

Calibration curves were obtained at both wavelengths (Figs. 3 and 4 respectively) and the relative sensitivities (for 1% absorption) and limits of detection are shown in Table 1.

TABLE 1.

Atomic Absorption and Emission of Mercury
at 253.7 and 184.9nm

Wavelength (nm)	Atomic Absorption		Atomic Emission
	Sensitivity (ppm)	Limit of Detection* (g)	Limit of Detection* (g)
184.9	0.2	4×10^{-11}	5×10^{-10}
253.7	8.0	3.2×10^{-9}	2×10^{-10}

* $S/N = 2.0$

The noise level at 253.7nm is approximately twice that at 184.9nm and in consequence the limit of detection at 184.9nm is better than expected from a comparison of the sensitivity ratio at the two lines.

The limits of detection for atomic emission at the same two lines are also shown in Table 1; however, in this instance the intercombination line at 253.7 gives the lowest limit of detection in spite of a higher noise level because the excitation energy required at 253.7nm is appreciably less than that at 184.9nm.

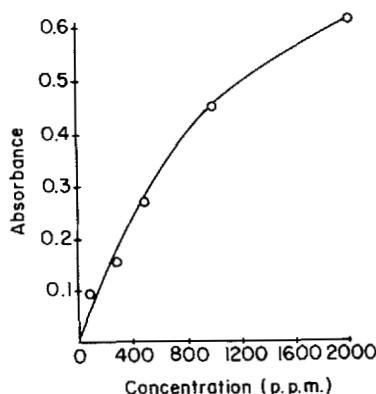


Figure 3. Atomic absorption of mercury at 253.7nm.

CONCLUSIONS

The determination of mercury by atomic absorption spectrometry at 253.7nm is now considered to be a standard method of analysis, especially as mercury may be atomised by virtually all types of non-flame cells; hence the atomic absorption method is normally preferred to that by atomic emission. Table I shows that the limit of detection by atomic emission at 253.7nm in an argon plasma can be superior to that by atomic absorption

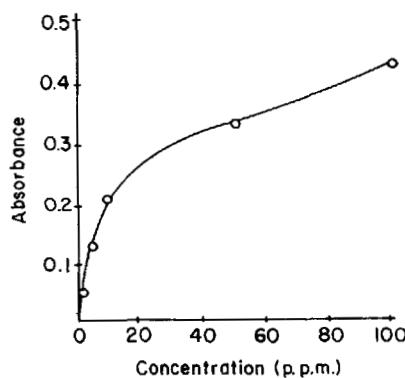


Figure 4. Atomic absorption of mercury at 184.9nm.

spectrometry. However, the lowest limit of detection may be obtained by atomic absorption spectrometry at 184.9nm. It is widely known that the 253.7nm intercombination ($6^1S_0 - 6^3P_1$) line is less sensitive than the resonance line at 184.9nm (3), in fact it is probable that the sensitivity at 184.9nm can be as much as 50-fold that at 253.7nm (1, 4). The results in Table I show a 40-fold increase in sensitivity which is sufficient to justify analytical determinations at the resonance line when increased sensitivity is required. A contributing factor in this work has been the utilisation of a mercury microwave excited electrodeless discharge lamp. It is relatively simple to prepare these sources for the more volatile elements such as mercury and they are quite stable in operation as a result of the production of essentially a "gas discharge". The intensity of the mercury discharge lamp is such that wavelengths can be monitored which up to this time have been considered to be beyond the reach of conventional non-vacuum instrumentation. The preparation of electrodeless discharge lamps for other volatile elements, e.g. S, P, halogens etc., which exhibit major resonance lines within the region 170.0 - 200.0nm, suggests that atomic absorption methods may be extended even further.

SUMMARY

The determination of mercury is described by atomic absorption and emission spectrometry at 184.9nm (resonance) line and 253.7nm (intercombination) line. A 40 fold increase in sensitivity by atomic absorption is observed at 184.9nm. A microwave excited electrodeless discharge lamp is used as source and the monochromator is purged with an inert gas.

REFERENCES

1. R.M. Dagnall, J.M. Nanfield, M.D. Silvester and T.S. West, Nature, 1972, 235, 156.
2. K.M. Aldous, R.M. Dagnall, B.L. Sharp and T.S. West, Anal. Chim. Acta, 1971, 54, 233.
3. W. Slavin, Atomic Absorption Spectroscopy, Interscience, New York, 1968.
4. H.G. Kuhn, Atomic Spectra, Longmans, London, 1964.

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