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AN AUTOMATED METHOD FOR THE DETERMINATION OF TOTAL MERCURY IN ENVIRONMENTAL SAMPLES

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ABSTRACT

Total mercury in environmental samples is determined by a continuous flow automated system capable of analysing 20 samples per hour. Any organic mercury present is first oxidised to inorganic Hg^{++}. A solution of Hg^{++} is presented to an automated system where it is reduced to elemental mercury by Sn^{++} and sparged from the solution into an AAS by continuous flow of air, to give equilibrium absorbance signals. The system is set up to give a linear working range up to 0.06 mg l^{-1} and a detection limit of 0.002 mg l^{-1}.

INTRODUCTION

The ubiquity of mercury in the environment coupled with its adverse toxicological effects has made the determination of this metal of great importance. This laboratory in its work of monitoring and surveillance of the aquatic environment analyses 3000-4000 samples each year for mercury. Samples arise from various sources and include industrial wastes, sediments and biota. It was therefore necessary to devise a method which would cope with a large number and diversity of samples and a broad range of mercury concentrations.

Most methods currently in use are based on the cold vapour/AAS technique proposed by Hatch and Ott (1968). This involves the chemical reduction of Hg^{++} with Sn^{++}, the elemental mercury being removed from the solution by a stream of air which gives rise to a transient Hg^{o} concentration. Improved accuracy has been obtained by establishing a partition equilibrium for Hg^{o} between the reduced test solution and a fixed volume of air, followed by measurement of the mercury content of an aliquot of this air, under static conditions (Stainton, 1971; Clinton, 1974; Kirkwood, 1976; Chapman and Dale, 1978). While these static measurement systems have much to commend them, they do not lend themselves readily to automation. Continuous flow systems have been described by El-Awady, Miller and Carter (1978) and Uthe (1972) wherein equilibrium partition conditions are achieved, thus retaining the benefits of the static systems while at the same time improving sample throughput. This paper presents an account of an easily constructed version of a continuous flow system.

MATERIALS

Apparatus

The general layout of the equipment is shown in Figure 1 and includes the following apparatus:

A Baird Atomic, model A3600, atomic absorption spectrometer (AAS). (A much older Southern Analytical, model A3000, has been used successfully.)

A Hook and Tucker, model A40, Sampler II auto-sampler with variable time controls for alternate sample/wash uptake, with turntable capable of accommodating 40 sample cups of nominal 8 ml capacity.

A Carlo Erba proportioning pump, model 1512/20.

An absorption cell constructed from borosilicate glass tubing 17 mm ID and 195 mm long, the single quartz window secured with epoxy resin.

A reactor/gas-liquid separator as shown in Figure 2.

An air pump of the type used by home aquaria.

A flow meter consisting of a graduated glass tube of 1.5 mm ID in which a metal ball is allowed to move freely.

A manifold arrangement as shown in Figure 1.

Reagents

Nitric acid, redistilled technical grade.

Hydrochloric acid, technical grade.

Stannous chloride, technical grade.

Potassium dichromate, analytical grade.

Hydrogen peroxide (120 vols), analytical grade.

Double distilled water.

Stock and working solutions

Stock Stannous Chloride - 200 g $SnCl_2$ dissolved in 500 ml HCl, final solution diluted to 1 l with double distilled water.

Working Stannous Chloride solution 5% W/V - Stock solution diluted by a factor of 4 with distilled water.

Solution 1 - 5% V/V HNO_3 and 0.05% W/V $K_2Cr_2O_7$ used mainly for maintaining Hg^{++} in solution (Carron and Altman, 1977). This is also used as the wash solution.

Working standards - serial dilutions of commercially available standard mercury solution (1000 ppm) (Hopkin and Williams Ltd) using Solution 1 as dilutant.

Glassware

All glassware is initially soaked for 12 hours in a detergent bath maintained at 40°C, then washed in water and soaked for a further 12 hours in 10% HNO_3 V/V and finally rinsed three times in double distilled water and dried in a warm air cabinet at 60°C.

METHODS

The organo mercury compounds present in the sample are first oxidised to inorganic Hg^{++}. This is achieved by digestion with a mixture of 1:1 HNO_3 and H_2O_2. Ideally 10 ml of HNO_3/H_2O_2 is added to a 5 g sample in a 50 ml tall form beaker with a glass cover. The mixture is boiled very gently until the volume is reduced to approximately 2 ml. The cooled residue is then diluted to 50 ml with Solution 1 and presented to the autosampler. This oxidative procedure has been proved capable of yielding complete recovery of Hg as Hg^{++} from CH_3HgCl, $(CH_3)_2Hg$ and various phenyl mercuric compounds. The total inorganic mercury is then reduced with stannous chloride to elemental mercury which is subsequently removed from the solution by a continuous stream of air. The absorption of the mercury containing air is quantified on its passage through the quartz-windowed absorption cell which is mounted on the AAS in place of the burner.

The instrument is first set up as follows:

Wavelength	253.7 nm
Slit width	0.25 mm
Source	Hollow cathode lamp

Chart speed	2 mm min^{-1}
Lamp current	2 mA

After optimising the alignment of the measuring cell in the light path of the AAS, a 0.04 mg l^{-1} standard (equal to 0.4 mg kg^{-1} in sample) is presented to the instrument. This is used to calibrate the instrument by adjusting the variable voltage on the potentiometric recorder so that a peak height of 40% full scale deflection (fsd) is achieved. The linearity of the instrument may be checked using standards at other concentrations. The samples are then placed on the autosampler with a standard as every fifth sample.

DISCUSSION

A typical recorder trace is shown in Figure 3 and a typical calibration curve is shown in Figure 4. By consideration of Beer's Law the sensitivity, and consequently the linear working range of the system, may be changed by adjusting the air flow rate.

As the system relies on equilibrium signals produced from a continuous flow system, and the same reagents are used both in the wash solution and in sample solution, moderate contamination from reagents can be accommodated because it will only result in an elevation of the base line. The signal due to mercury in the samples and standards will simply be superimposed on the elevated base line.

The need for a more sophisticated AAS with double beam and background correction system has been found to be unnecessary. Baseline drifts during lamp warm-up time are obviated by leaving the AAS on continuously. Non-specific absorption due to molecular species has been studied. Samples were passed through the system without the reductant and under these conditions no absorbance signals were produced. The presence of water vapour in the system did not enhance the absorbance signals; this has been confirmed by Stuart (1978). The effect of the matrix on partition coefficient between gas and liquid was investigated using the method of standard additions and synthetic matrix, but no effect on absorbance signals due to the matrix could be detected. Results by standard additions were the same as those obtained using samples analysed in the usual manner.

CONCLUSIONS

This system has been used successfully by the laboratory over the last three years. It is relatively trouble-free and does not require the use of skilled technicians. Its high sample throughput and immunity against simple matrix interference makes it invaluable in a laboratory analysing large numbers of environmental samples.

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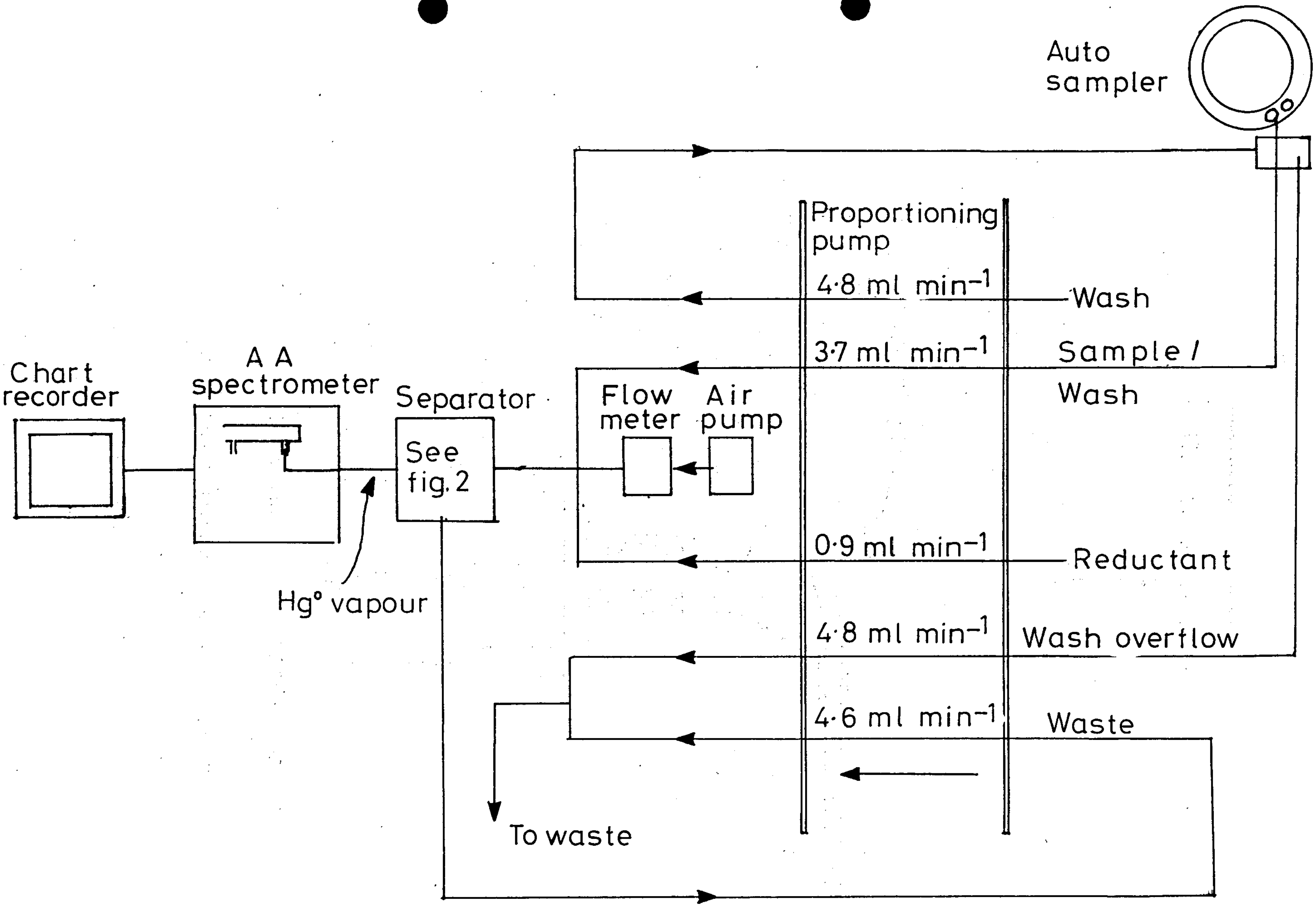

Figure 1 Schematic diagram of mercury manifold.

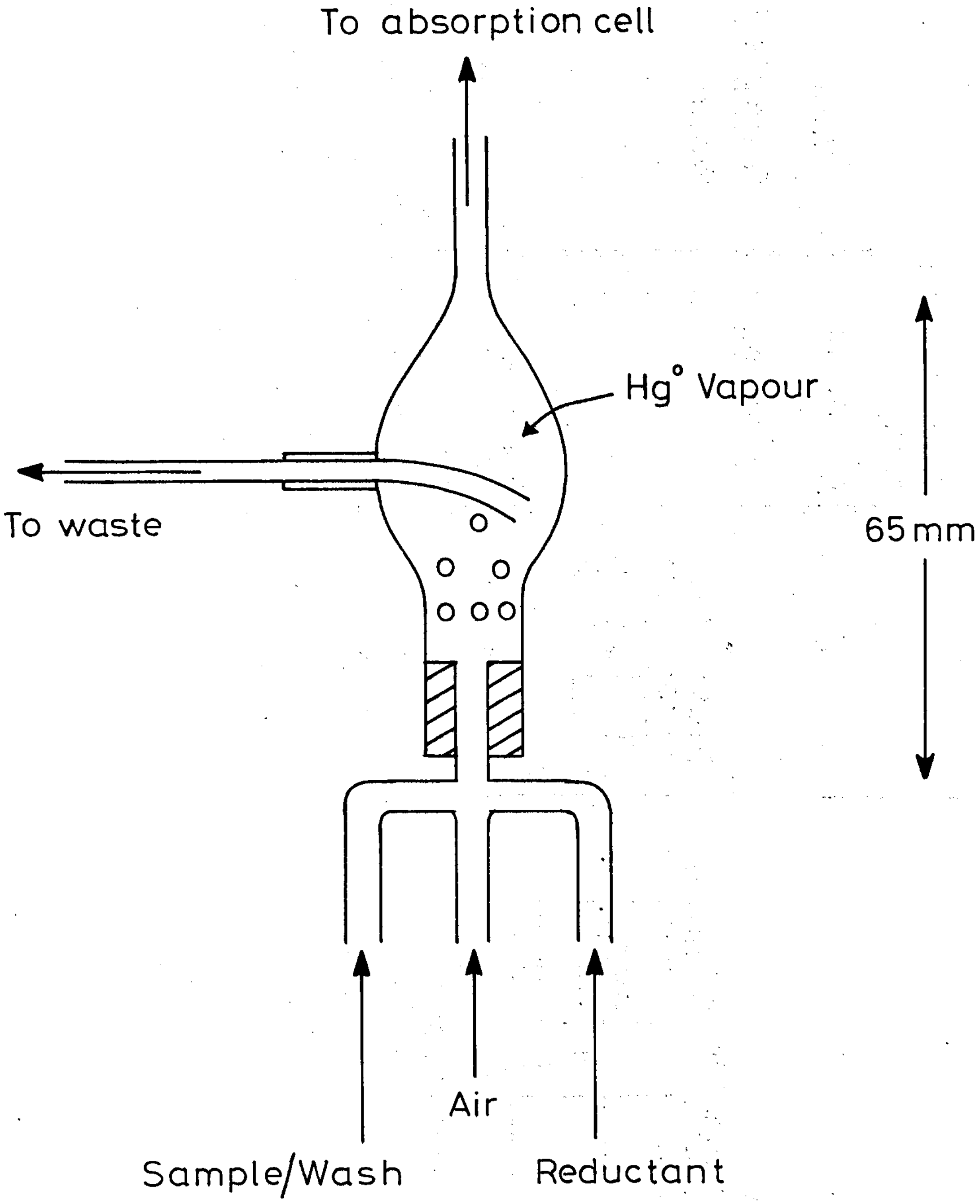

Figure 2 Reactor/gas-liquid separator.

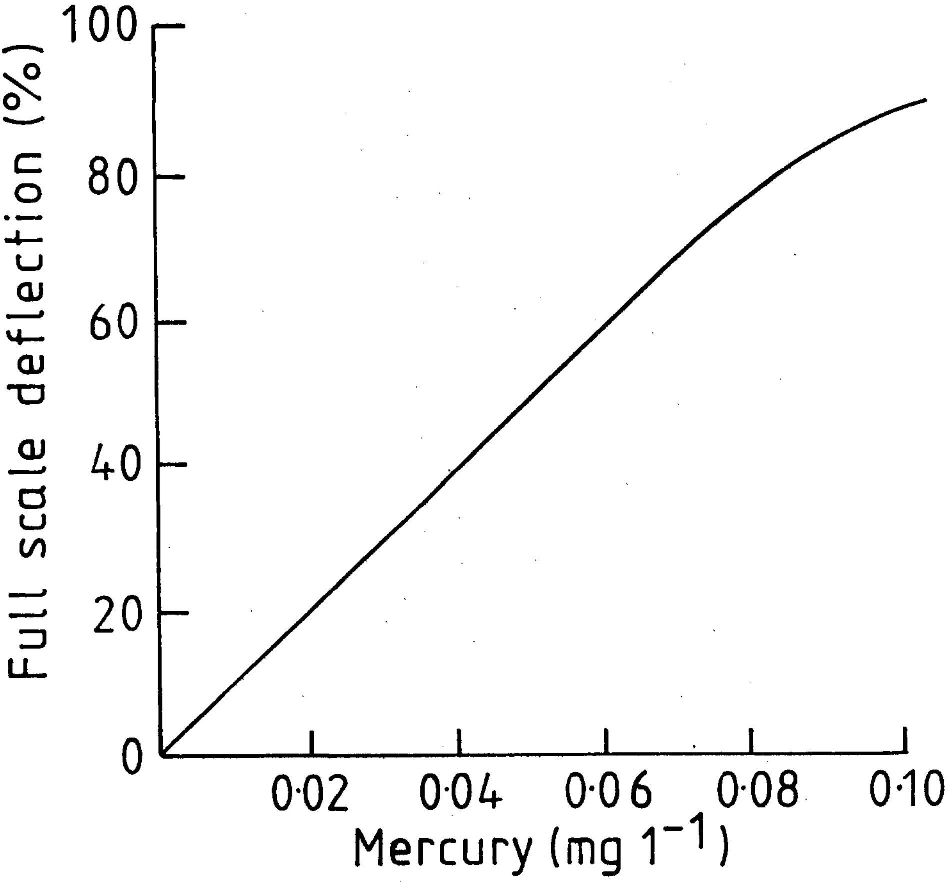

Figure 3 Typical calibration curve.

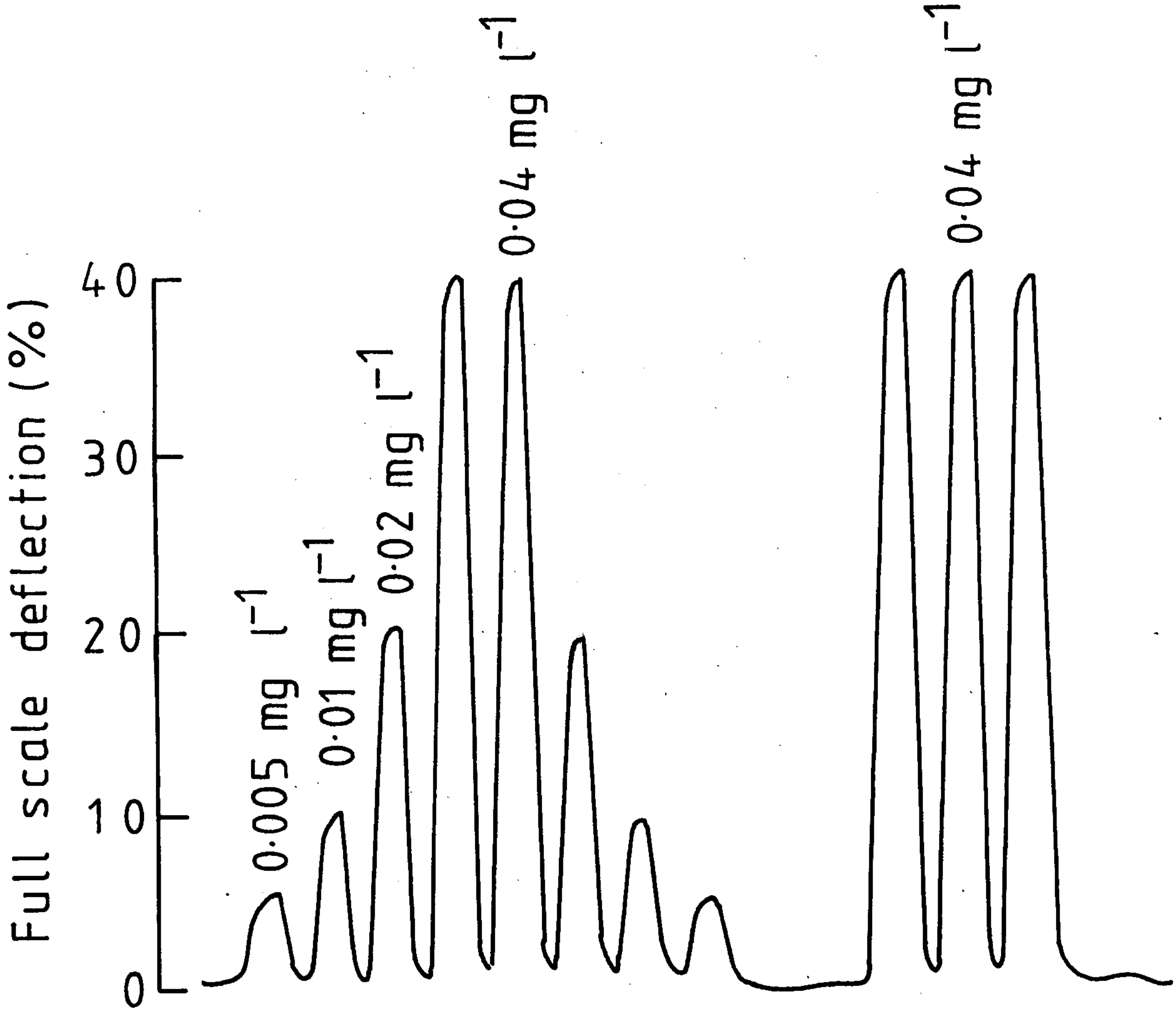

Figure 4 Recorder plot with standard mercury solutions.