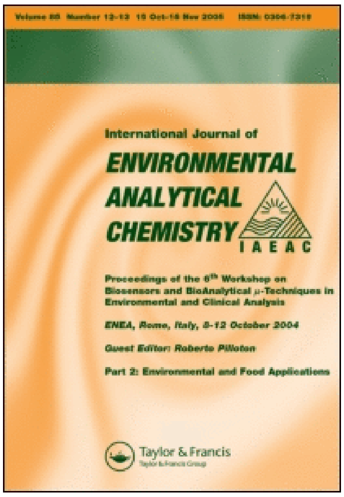

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The Collection and Analysis of Mercury from Mercury Cell Chlor-Alkali Plant Gaseous Process Streams

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Recently National Emission Standards Regulations were promulgated for mercury from chlor-alkali plants in Canada using the mercury cell process. The amount of mercury emitted to the ambient air can be measured by the Standard Reference Methods for Source Testing: Measurement of Emissions of Mercury from Mercury Cell Chlor-Alkali Plants. This paper presents data accumulated during the development of the sample collection and analysis methods described in the above publication. The accuracy of the combined collection and analysis methods is estimated to be ±5%. The sensitivity of the method is estimated to be 10 ng of mercury in the flameless atomic absorption analysis system. Levels of mercury as low as 1 $\mu g/m^3$ are detected. The method is specific for mercury in its elemental and inorganic forms in the gaseous process streams described in the standard reference method. Organic mercury compounds were not considered to be emitted by the chlor-alkali industry. The precision of sample analysis was estimated to be ±1.6%.

KEY WORDS: Mercury, chlor-alkali, emissions.

INTRODUCTION

Regulations[1] for mercury emissions from mercury cell chlor-alkali plants,[1] enacted under the Clean Air Act of Canada, specify that mercury be measured using the Standard Reference Methods for Source Testing: Measurement of Emissions of Mercury from Mercury Cell Chlor-Alkali Plants.[2] This paper describes the development work and rationale associated with the reference method.

Mercury from a chlor-alkali plant is emitted in a variety of gaseous process streams. It is found in the by-product hydrogen which is vented to the atmosphere or burned as fuel even though most plants remove large amounts of mercury before the release of hydrogen to the atmosphere. Mercury is also present in the working atmosphere of the cell room which is usually vented unfiltered to the ambient air. Gases exhausted from end boxes, retorts and storage tanks during normal operations are also significant emission sources. All but the hydrogen stream, which is essentially pure hydrogen, are considered streams of mercury in air. It is not within the scope of this paper to detail the plant operations which result in mercury entering the process streams, since information is readily available in the liteature.[3,4] Most of the mercury emitted from chlor-alkali plants is in the elemental vapor form,[5,6] which predominates over the aerosol form, if the latter exists at all. Organic mercury compounds are not effectively collected by the method described,[7] but are probably absent from chlor-alkali plant gaseous streams and consequently were not examined during this study.

Briefly, the method requires that the gas being analyzed be bubbled through an impinger containing 200 ml of 2% potassium permanganate in 10% sulfuric acid, whereby mercury is trapped by impingement and oxidized to the mercury (II) form. After collection, excess permanganate is reduced with hydroxylamine and the solution is transferred to a volumetric flask. An aliquot is further reduced with stannous chloride to convert the oxidized mercury back to the elemental form which can then be aerated into a flameless atomic absorption analysis system.

The origin of the use of acid permanganate solutions to collect mercury from air by impingement is uncertain, but probably derived from the use of acid permanganate to minimize digestion losses in the classic dithizone method for mercury determination.[8] Dow Chemical Company has published an analytical method based on the use of permanganate.[9] One other reagent, iodine monochloride, has been used extensively to capture airborne mercury by impingement. This was the method designated in the United States Environmental Protection Agency's promulgation of emission regulations for the chlor-alkali industry.[10] The method has recently been updated and now imposes closer tolerances on operating conditions and equipment design.[11] The analysis of collected mercury, as with the Canadian standard reference method, was based on flameless atomic absorption.[12]

Collection of mercury on solid absorbers such as noble metals, Hopcalite or carbon does not lend itself well to the high levels of mercury and chlorine encountered in the chlor-alkali plant environment.[7] Reliable instruments for direct ultraviolet measurement of the mercury in chlor-alkali plants are not available commercially but a prototype instrument was used in connection with this work and performed satisfactorily in the laboratory.[13]

EXPERIMENTAL WORK AND RATIONALE

Apparatus

Two atomic absorption units were used. One was a Perkin–Elmer 403 equipped with the manufacturer's kit for conversion to flameless atomic absorption analysis of mercury using an optical cell. The other, a less sensitive, portable instrument suitable for field use, was a Coleman 50 mercury monitor equipped with a similar optical cell. The sample analysis systems of both instruments consisted of a pump to circulate air through the optical cell and the 250–300 ml sample bottle containing the aerator. Figure 1 is a diagram of this equipment showing some of the important features. Parameters for the operation of the atomic absorption instruments were as supplied by the manufacturers. No attempt was made to alter these parameters as sensitivity was adequate and our investigations were centered on the handling of standards and samples to achieve maximum stability. It was not necessary to place a desiccant in line before the absorption cell and the levels of mercury in the laboratory air did not interfere with the analysis. Absorbance readings from the Perkin–Elmer 403 were "100 average" readings, the average of 100 absorbance readings taken over a 10 second period. The Coleman 50 had a memory feature

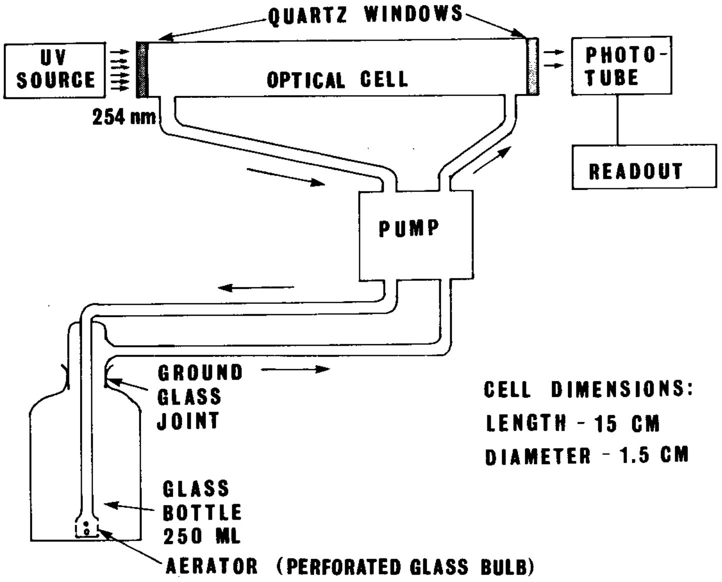

FIGURE 1 Aerator and flameless atomic absorption system.

which held the maximum absorbance achieved during a measurement. An aeration flow rate of three litres per minute (factory-set by Perkin–Elmer) was used. The Coleman 50 also used an aeration flow rate of three litres per minute.

The same sample bottle was used for all analyses and was rinsed three times with tap water followed by three rinses with distilled water between samples. Non-reproducible results were obtained when more than one sample bottle was used.

An instrument designed and built in our laboratory[13] was used to monitor impinger collection efficiency and to evaluate the dynamic mercury source used in this work. This instrument was calibrated with a static mercury source by syringe injection of known volumes of mercury-saturated air into the optical cell. The dynamic source of mercury was designed to generate mercury in the 0–3000 $\mu g/m^3$ range. This system, built in our laboratory, was similar to those described by Nelson[14] and Scheide *et al.*[15] The source produced steady mercury concentrations which agreed with the independently calibrated ultraviolet mercury monitor and standard mercury salt solutions used for atomic absorption calibration.[16]

The impingers used for mercury collection were the Greenburg–Smith type connected in series using ball and socket U-connectors. In the laboratory, mass flowmeters were used to measure the flow through the impingers which were connected to a manifold system on the dynamic source. Flow measurements in the field were performed using the standard reference method.[17] Figure 2 shows the laboratory equipment used for mercury in air generation and Figure 3 shows the collection apparatus.

Mercury collection

Our initial work with the method indicated that the instability of both mercury and permanganate in solution were factors contributing to variable non-reproducible results. Acid permanganate, while being a good medium for trapping mercury, is easily reduced to manganese dioxide and eventually to a colorless solution of manganese ions. This decomposition is catalyzed by light and auto-catalyzed by manganese dioxide itself. In addition dilute mercury standards are notoriously unreliable, even in an acid permanganate solution, due to the volatility of mercury and its affinity for the wall of the containers in which it is stored. It was assumed that decomposition of the permanganate would accelerate as soon as gas was bubbled through the impinger and therefore it was imperative to use freshly prepared permanganate daily. No effort was made to remove manganese dioxide inevitably formed during the preparation of the

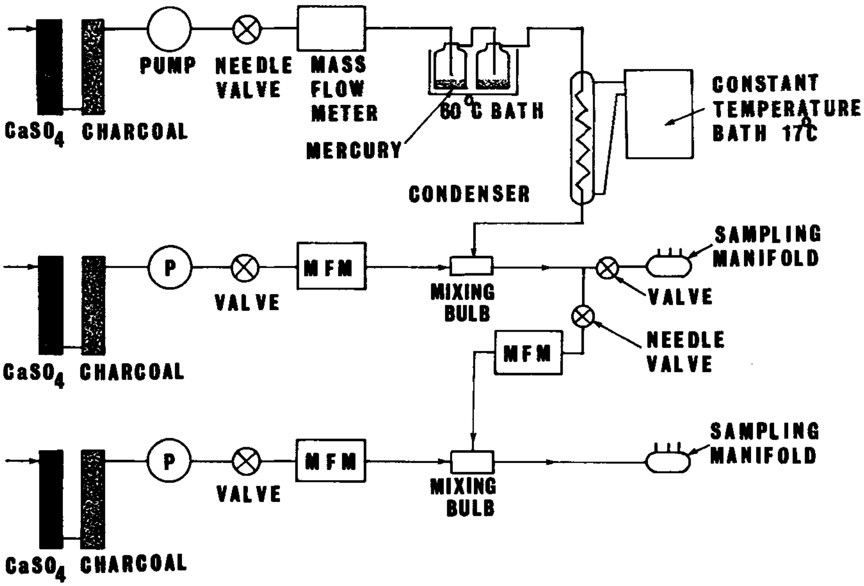

FIGURE 2 Dynamic mercury calibration source.

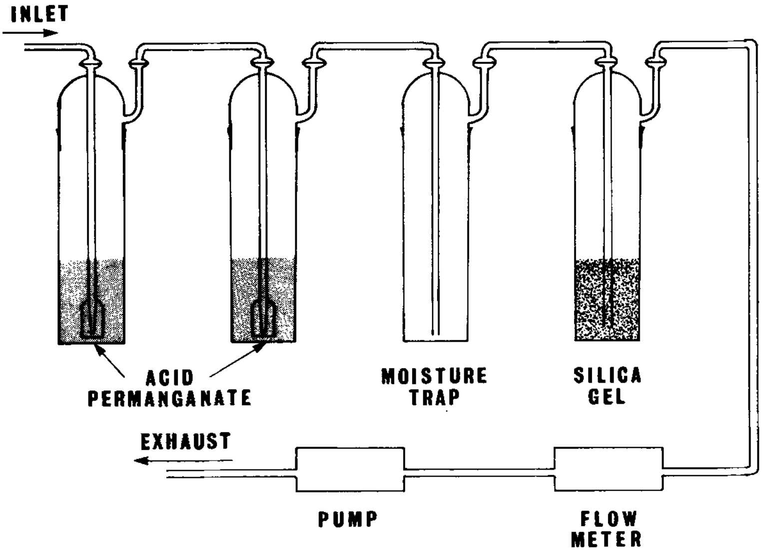

FIGURE 3 Mercury collection apparatus.

permanganate. All manganese dioxide was redissolved when excess permanganate was reduced with hydroxylamine after collection and had no detectable effect on collection of efficiency. In order to save time in the field and for safety reasons it was recommended that the sulfuric acid for the collection reagent be diluted to 20% v/v (twice the working strength) in the laboratory. Thus in the field it was only necessary to dissolve a preweighed amount of permanganate in acid solution and dilute to form a solution containing 2% of permanganate in 10% sulfuric acid.

The results of tests made in the field and laboratory indicated that more than 95% of the mercury collected was in the first impinger (Tables I and II). These studies were made at mercury levels up to 50,000 $\mu g/m^3$. The overall efficiency of collection was examined by placing the mercury monitor in line after the second impinger containing permanganate. The detection limit of this instrument was 10 ng of Hg (corresponding to a 10 ml aliquot of 1 ng/ml Hg standard). No mercury was observed passing through the impingers.

A comparison of mercury concentrations generated by the dynamic source, and measured with the mercury monitor, and concentration measurements made using the standard reference method[2] showed them to agree within 8%. As neither the dynamic mercury source nor the mercury monitor was an integral part of the standard reference method, the results obtained using them were useful only as an indicator of the accuracy of the collection and analysis procedures. Assuming that all the mercury has been collected using two impingers, these results point to a possible loss of sample during the transfer, reduction and analysis steps. As a result, samples and standards were treated in as similar a manner as possible to minimize the effect of any loss of mercury while in the reduced state.

Collection times between fifteen minutes and four hours were examined. This range of time permitted enough flexibility to allow for the collection of mercury from any of the gas streams in sufficient quantity for atomic absorption analysis. The longer sampling times would be associated with the cell room concentration, usually below 200 $\mu g/m^3$. No loss of mercury was detected from the impingers after four hours of sampling when monitored with the mercury monitor. However, some loss was anticipated over longer sampling periods as the oxidizing power of the permanganate was lost.

Sampling rates between 1–2 litres per minute were used in laboratory studies and there was no detectable effect of flow rate on collection efficiency. During field tests, sampling rates up to 3 litres per minute over a wide range of mercury concentrations again produced no detectable effect on collection efficiency. It was concluded that collection rates

TABLE I

Laboratory studies of collection efficiency

Approximate mercury concentration generated ($\mu g/m^3$)	Mercury concentration 1st impinger (ng/ml)	Mercury concentration 2nd impinger (ng/ml)	% in first impinger
3000	750	14	98.1
3000	1280	17	98.7
150	110	2	98.2
150	275	5	98.2
150	270	3	98.9
150	96	B	~100.0
150	218	3	98.6
3000	700	18	97.4
3000	670	20	97.0
3000	700	22	96.9
150	38	3	92.1
150	43	4	90.7
180	46	4	91.3
2500	350	15	95.7
2500	650	24	96.3
2500	353	18	94.9
1500	282	15	94.7
1500	282	23	91.8
1000	205	6	97.1
1000	223	5	97.8
1000	217	4	98.2
1000	100	3	97.0
1000	113	3	97.4
1000	115	4	96.5
1000	225	2	99.1
1000	50	B	~100.0
1000	52	B	~100.0
1000	46	B	~100.0
1000	60	3	95.0

B below detection limit.
1. Mean collection efficiency of the first impinger is 96.8%.
2. Standard deviation of mean collection efficiency is ±2.6%.

between 1 and 3 litres per minute could be used, a sufficiently wide range to permit the operator to maintain a sampling rate proportional to the stack gas velocity throughout the sampling period.

Mercury standards

One of the first steps in the method development work was the exam-

TABLE II

Field studies of collection efficiency

Mercury concentration measured (μg/m^3)	Mercury concentration		% in first impinger
	1st impinger (ng/ml)	2nd impinger	
85	158	10	93.7
95	172	14	91.9
79	288	20	93.1
170	800	90	88.8
381	1980	220	85.9
296	1540	50	96.8
58	104	B	~100.0
57	174	10	94.3
81	214	8	96.3
73	166	12	92.8
153	650	90	86.2
312	1640	50	97.0
209	1210	0	~100
93	400	20	95.0
96	380	40	89.5
41	86	0	~100
45	94	0	~100
104	200	8	96.0
78	144	10	93.1
90	445	0	~100
226	1020	70	93.1
117	400	140	65
59	118	0	~100
63	124	0	~100
62	226	18	92.0
200	960	60	93.8
497	2500	20	99.2
258	1280	20	98.4
66	220	0	~100
88	300	40	86.7
10,397	26,800	50	99.8
8,949	11,700	B	~100
9,030	16,400	B	~100
12,540	14,400	0	~100
12,722	15,000	40	99.7
30,613	28,300	60	99.8
49,826	79,500	180	99.8
25,167	32,400	150	99.5
25,620	32,400	170	99.5

B below detection limit

1. Mean collection efficiency of the first impinger is 95.3%.
2. Standard deviation of the mean collection efficiency is ±6.6%.

ination of mercury standards prepared by a variety of reagents. Figure 4 shows the results of studies at two mercury concentration levels. To match the collecting medium it was intended that standards be prepared in a solution of potassium permanganate and sulfuric acid in water. However, the remarkable stability of mercury standards prepared in a nitric acid/potassium dichromate solution relative to those in acid permanganate or water prompted us to test the dichromate solution further. It became apparent, however, from a comparison of standard curves prepared in dichromate and in permanganate solutions that the matrix had a pronounced effect on response (Figure 5). It was concluded that standards must be prepared in the same reagent used for collection. This may apply to other mercury measurement situations using flameless atomic absorption as well. Therefore the mercury standards consisted of mercuric chloride in freshly prepared 2% $KMnO_4$/10% H_2SO_4.

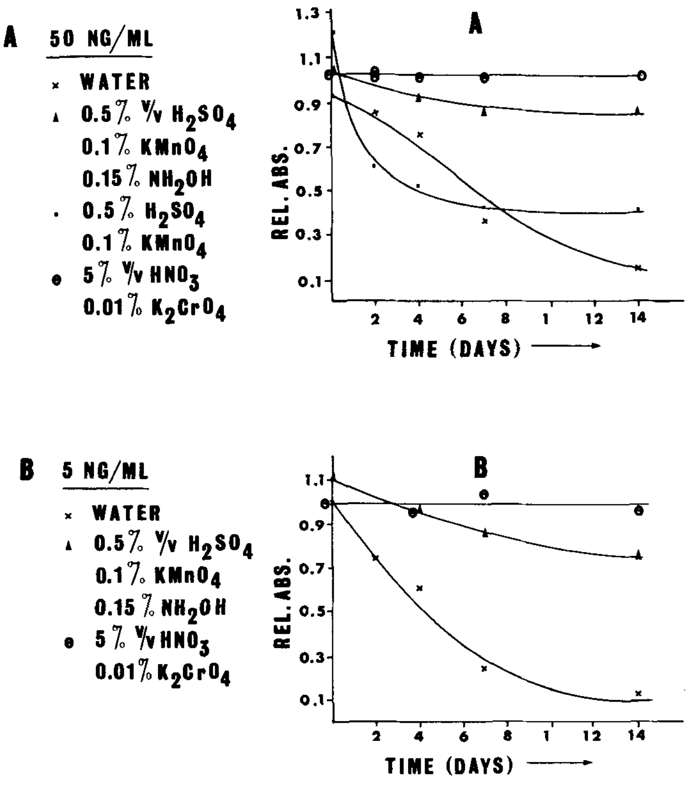

FIGURE 4 Stability of mercury standards in various reagents.

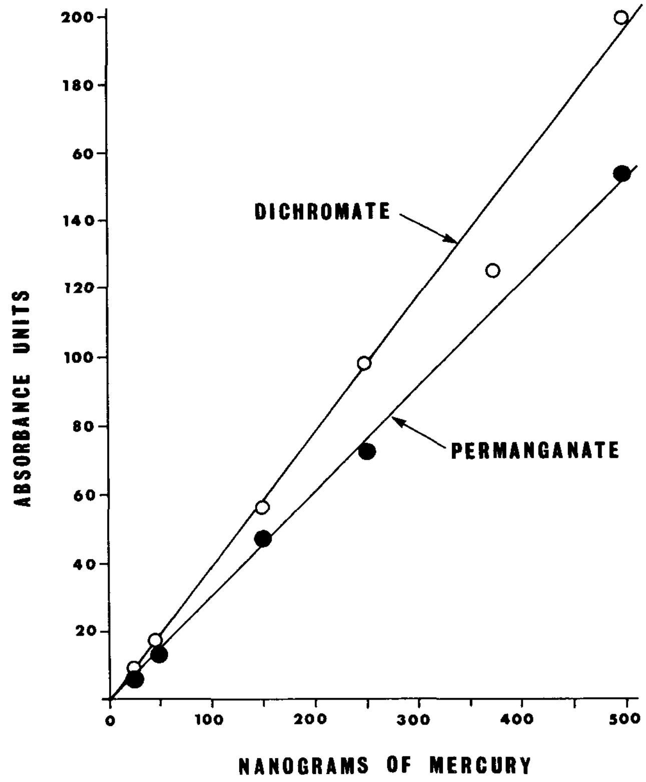

FIGURE 5 Calibration curves for mercury in permanganate and dichromate solutions.

The stability of mercury standards in the collection reagent was examined using working standard concentrations of 100 and 500 ng/ml. Standards stored in the acid permanganate were compared with standards prepared freshly on an hourly basis. Studies over a 20-hour period indicated no change in absorbance with time. On the other hand, standards stored in a reduced acid permanganate solution were extremely unstable (Figure 6). It was assumed that samples and standards behave similarly and we concluded that all samples and standards should be analyzed within one half hour of the addition of hydroxylamine. *This time limit confined losses from solution after reduction to a maximum of* 5%, although our experience has shown that an analysis can easily be performed within five minutes of the addition of hydroxylamine. In the latter case, losses should not exceed 1% and are probably negligible if samples and standards are treated in the same manner.

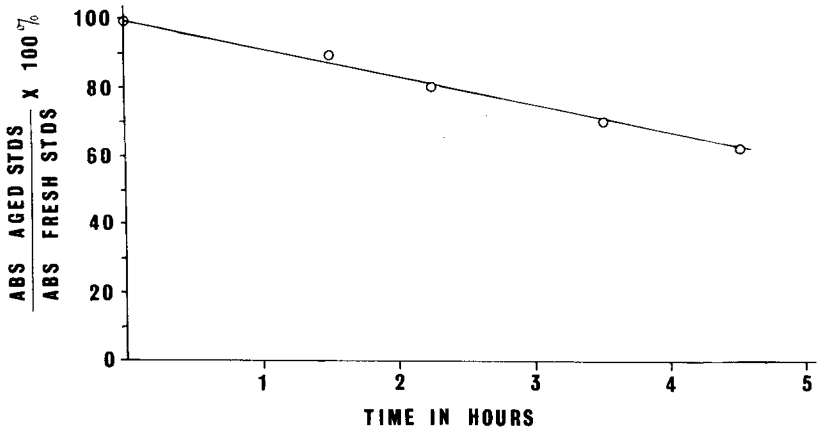

FIGURE 6 Loss of mercury from reduced permanganate (2% $KMnO_4$ in 10% H_2SO_4 reduced with NH_2OH).

The preparation of working standards in the 0–500 ng/ml range from 1000 ppm stock mercury standards was achieved by a two-step dilution, i.e., through an intermediate standard of 10 ppm. The stabilities of the three concentrations of standards were found to be at least three months for the 1000 ppm standard, one week for the intermediate standard of 10 ppm mercury in 1% v/v HNO_3 and one-half hour for working standards in acid permanganate. The working standards were prepared by adding 80 ml of acid permanganate to a 100 ml volumetric flask, adding 1 ml of 10 ppm mercury in 1% v/v HNO_3 and reducing the permanganate with a minimum amount of 15% hydroxylamine hydrochloride. Aliquots of 1, 2, 3, 4 and 5 ml containing 100, 200, 300, 400 and 500 ng of mercury respectively were added to the sample bottle containing 100 ml deionized water and were analyzed by the flameless atomic absorption method within one half hour of the addition of hydroxylamine. This procedure was shown to be as accurate as and much faster than preparing a range of individual working standards. The calibration step thus requires a minimum expenditure of time. This is important for a field method where standards must be prepared fresh daily.

The response was linear between 0–500 ng of mercury in the atomic absorption analysis system (Figure 7). Although the atomic absorption method can be used above 500 ng, it was calculated (Figure 8) that for the collection times and sample flow rates indicated in the standard reference method,[2] the amount of mercury per ml of collection reagent would fall in the 0–500 ng/ml range for mercury concentrations in the process streams below 2000 $\mu g/m^3$. This covered cell room concentrations during normal operation and well-controlled stack emissions. When mercury concentrations were greater than 500 ng/ml, small aliquots and/or an extended range of standards were used.

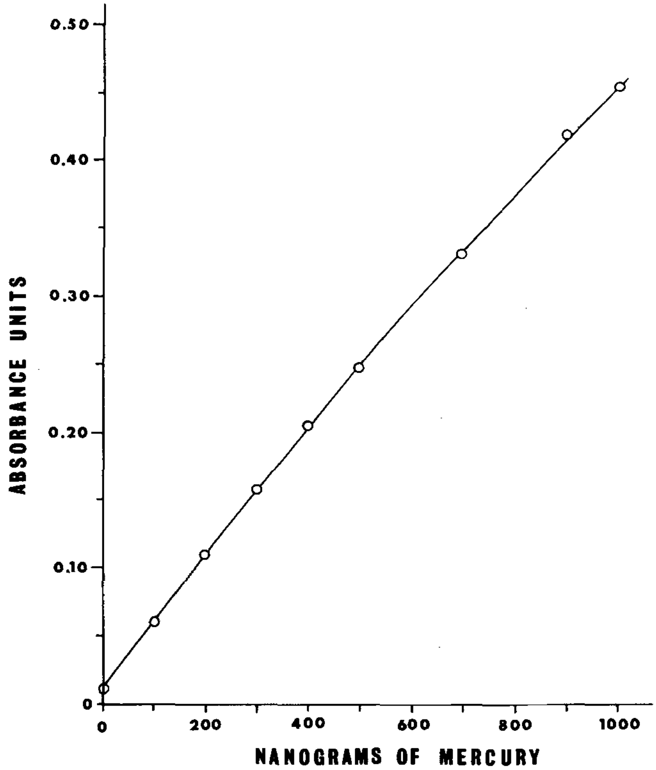

FIGURE 7 Response of mercury standards.

Mercury analysis

A 15% w/v hydroxylamine hydrochloride solution was found to be convenient for the transfer of the acid permanganate from the impinger to the volumetric flask. It dissolves any manganese dioxide (formed from the decomposition of permanganate during collection) adhering to the glass surface of the collection system. A *minimum* amount of hydroxylamine solution is used in order not to exceed the 250 ml capacity of the volumetric flask. The transfer was completed with water.

The reduction steps proved to be the most important in the entire method. Premature reduction of collected mercury or mercury standards can occur through the addition of the hydroxylamine used to reduce excess permanganate. Mercury standards which had been reduced with hydroxylamine and then analyzed were shown to give absorbance readings equal to standards treated with both hydroxylamine and stannous chloride, although in the former case a long aeration period was required. Unwanted reduction of mercury can also occur when reducing agents are present as impurities in standards or samples. Aeration of mercury standards in acid permanganate solution to which no reducing agent has been added failed to liberate mercury from solution. The point of addition of hydroxylamine was considered to be the critical step, since at that point the mercury reduction starts and the unstable elemental mercury begins to form.

DISCUSSION

The reliability of the method was assessed by determining accuracy, precision, sensitivity and specificity.

Any substance affecting the specificity must (a) be collected by impingement in acid permanganate, (b) be capable of being aerated out of solution into the absorption cell, and (c) be capable of absorbing radiation at 253.7 nm. Among the fumes present in a chlor-alkali plant atmosphere there may be sodium chloride, sodium hydroxide and chlorine gas. The absorbances of standards to which 0.5% sodium chloride and 0.5% sodium hydroxide had been added were unaffected by the presence of the salts. Chlorine gas, present in the solution in saturation amount gives no response at the analytical wavelength.

The sensitivity of the method is determined by the minimum amount of mercury which must be present in the sample bottle (Figure 1) to produce a statistically significant response when aerated out of solution. This amount was found to be 10 ng of mercury. Using the standard reference method, concentrations in the atmosphere of 1 $\mu g/m^3$ could easily be detected.

The precisions of absorbance measurements (6 determinations) made at the 50 and 500 ng of mercury (in the sample bottle) levels were found to be ±1.5% and ±1.6% respectively for standards prepared as described in the standard reference method. The precision of the combined sample collection and analysis procedures was not easily assessed as laboratory sources of mercury showed some variation in concentration with time due to slight changes in parameters such as ambient temperature and atmospheric pressure over the analysis period. In the field, these variations and fluctuations in mercury concentration are such that a precision study would merely reflect these concentration changes, rather than the precision of the measurement.

Inaccuracies inherent in the sampling and analytical procedure have been minimized by prescribing the preparation of working standards in acid permanganate of the same composition as that used for sample collection. The conversion of elemental mercury to mercury II was judged to be complete because aeration of collected samples, without prior addition of any reducing agent, failed to induce instrument response. The best accuracy achievable, really an expression of the expected inaccuracy of the mean value, is ±5%. This is a total of the inaccuracies expected at the various stages of the analysis estimated as follows: (a) collection efficiency, negligible for two impingers; (b) oxidation ($Hg^0 \rightarrow Hg^{++}$), negligible; (c) transfer losses (reduction), 2.5% (if analyzed within 15 minutes of hydroxylamine addition); (d) transfer losses (volumetric), 1%; (e) preparation of standards, 1% and (f) unaccounted errors, 0.5%.

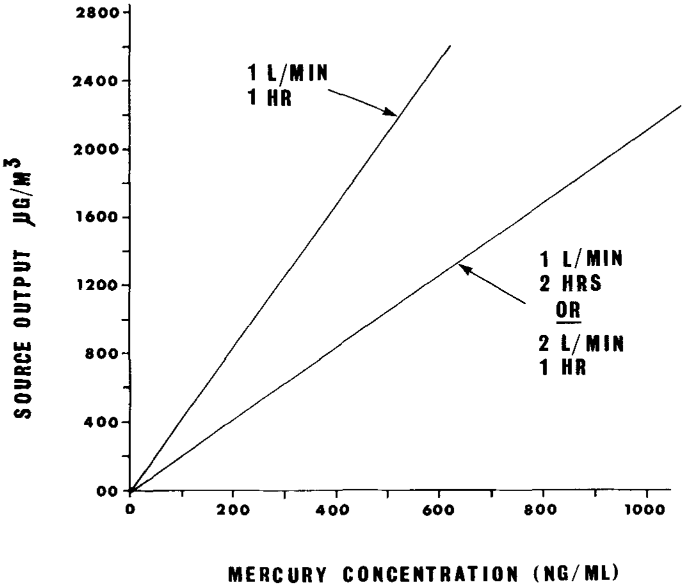

FIGURE 8 Source strength vs final mercury concentration.

Acknowledgements

The authors wish to acknowledge the contributions of Mr. G. Dowd of the Chemistry Division, who provided and calibrated the mercury monitor; the members of the Surveillance Division, Air Pollution Control Directorate, who collected the field samples; and the technical assistance of Mr. Brian McDonnell in the initial work on stability of standards.

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