THE GAS CHROMATOGRAPHIC DETERMINATION OF TETRAETHYLLEAD IN AIR

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Tetraethyl- and tetramethyllead are highly toxic compounds and their concentration in the atmosphere near the places where they are produced or handled should be strictly controlled. Routine determinations are usually carried out by passing the air to be analysed through adsorbing solutions and the lead concentration is measured by some colorimetric methods. BYTHOVSKAYA[1] measured small amounts of tetraethyllead (TEL) in air by reaction with silver nitrate. SNYDER et al.[2] used an iodine solution as absorbing medium and a colorimetric method with dithizone for the quantitative determination. NAGASAWA AND FUNAKUBO[3] removed the TEL from air with iodine in carbon tetrachloride and LINCH et al.[4] employed iodine in methanol similarly.

The use of a reactive solution for collecting small amounts of organic lead from the atmosphere is limited by the volatility of the reagents or solvents, and slow flow rates for long sampling periods should be adopted to obtain quantitative results. Gas chromatographic methods can be successfully adapted for the separation and determination of the alkyl leads.

BONELLI AND HARTMANN[5] and DAWSON[6] directly determined tetraethyl- and tetramethyllead in gasoline in a few minutes, by means of the specific and highly sensitive electron capture detector.

In this paper a procedure is described for the direct collection of TEL from polluted air and its gas chromatographic determination at p.p.m. levels.

In this method the principle described by JANAK et al.[7] is used for measuring very small amounts of volatile pollutants in the air by gas–liquid chromatography. The method consists in passing the air to be analysed through a short column, packed with the usual gas chromatographic support and liquid phase, which acts as a sampling tube. When enough air has been passed through to saturate this column, an equilibrium is established between the concentration in the gas phase (C_g) and the concentration in the liquid phase (C_l) of the compound to be determined.

The partition coefficient $K = C_l/C_g$ is known from the relationship for the specific retention volume:

$$K = V_g \rho \frac{T}{273}$$

and by substitution:

$$C_g = \frac{C_l\ 273}{V_g \rho T}$$

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Since the concentration in the liquid phase can be expressed by:

$$C_l = \frac{m}{w/\rho}$$

the following equation is obtained:

$$C_g = \frac{m \, 273}{w V_g T} \tag{1}$$

where w is the amount of liquid phase in the sampling tube and V_g is the specific retention volume of the compound to be determined at the temperature T of the sampling tube. The amount m of this compound contained in the sampling tube is measured by injecting the collected sample directly into the gas chromatograph.

In this way the concentration C_g of the compound in the air under analysis is obtained from eqn. (1).

EXPERIMENTAL

A Carlo Erba gas chromatograph (model PAID/f) was used with an electron capture detector. The column was prepared from a glass tube 0.3 mm I.D. and 1 m long, packed with Chromosorb P 80–100 mesh containing 10 % of silicone rubber SE-52. The other working conditions used for the determination of TEL are as follows: oven temperature 80°, injector and detector temperature 130°.

Carrier gas was pure nitrogen with an inlet pressure of 1 atm and a flow rate of about 30 ml/min. An additional stream of nitrogen at 150 ml/min is passed directly through the detector to reach the optimum value for the detector sensitivity. The response of the electron capture detector for the alkyl leads is greatly affected by the applied potential. In Fig. 1 the detector current is plotted for various applied potentials (curve A), and the detector response (curve B) measured in arbitrary units from the peak areas for the same injected amount is also shown.
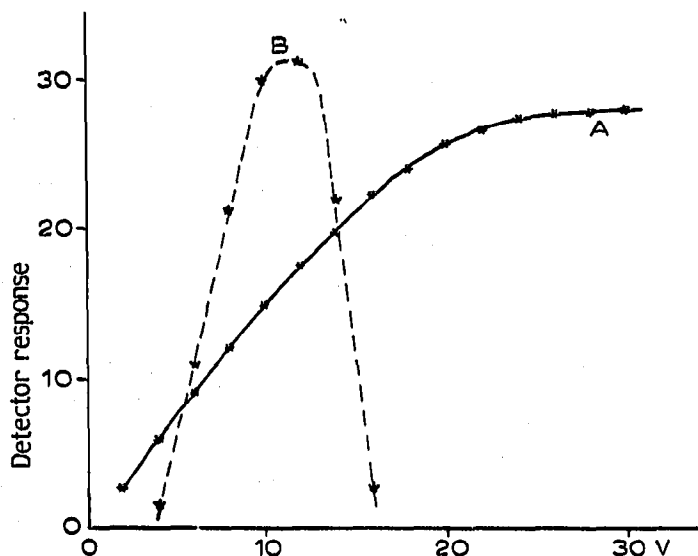

Fig. 1. Electron capture detector plots of current (A) and response (B) versus applied potential.
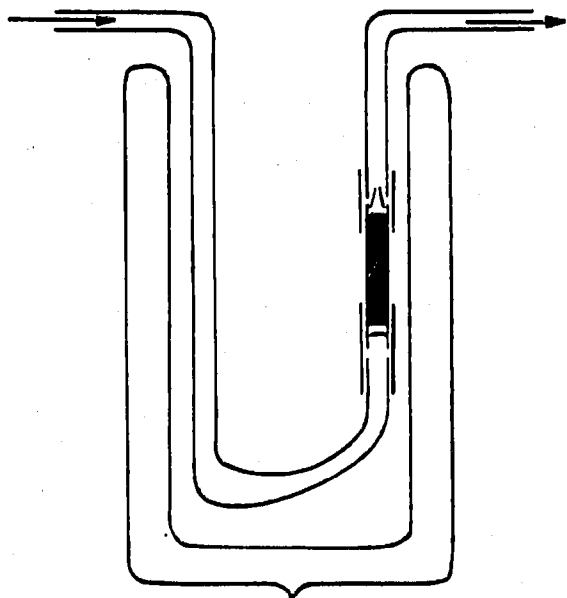
Fig. 2. Sampling apparatus for collecting TEL from polluted air.

As seen in Fig. 1 the maximum response is obtained at about 12 V, where the detector current is about 65 % of the saturation current.

These curves were periodically checked and although the detector current changes with the working conditions the maximum response was always found at about 65 % of the saturation current.

Sampling apparatus

The sampling tubes were prepared from 1 ml hypodermic syringes about 8 cm long and 0.5 cm I.D. To collect the samples, air is passed through this tube by suction with a small pump (C. Austen mod. DYMAK II) with a flow rate of 1.5 l/min for 10–15 min.

The collection of the samples was carried out either with the tube at ambient
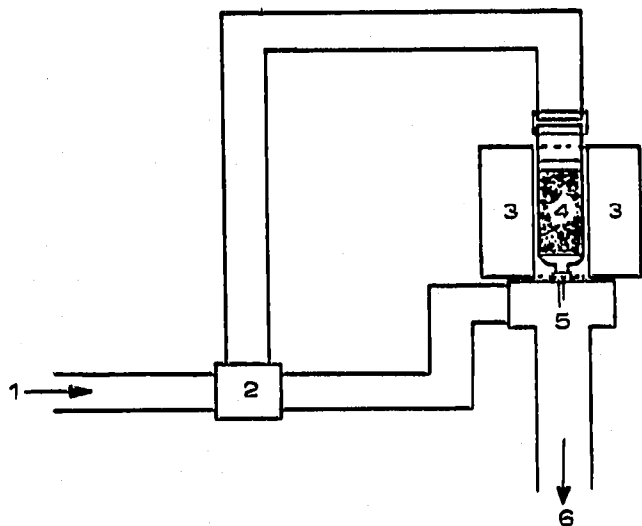

Fig. 3. Injection system for the introduction of the collected samples into the gas chromatograph. 1 = Carrier gas inlet; 2 = 3-way stopcock; 3 = heater; 4 = sampling tube; 5 = injection port; 6 = column.

temperature or at 0° (in ice) as shown in Fig. 2. The air before entering the sampling tube passes through an empty U-tube where the excess of atmospheric water condenses. The injection system shown in Fig. 3 was used to measure the amount of TEL trapped in the sampling tube by gas chromatography.

The carrier gas (1) can pass either directly from the stopcock (2) through the chromatographic column or through the sampling tube. For introduction of the sample this tube (4) is flash heated to about 130° by a small electric furnace (3) positioned immediately above the injection port (5).

After heating the syringe is pushed so that the needle passes through the silicone rubber septum; by rotating the stopcock (2) the carrier gas flushes the sample into the chromatographic column and the TEL peak is recorded.

Spectrophotometric measurements were performed at the same time with an automatic apparatus (Terzano mod. DP/1). The air was filtered through a Whatman No. 1 filter paper and drawn through a series of scrubbers consisting of 0.1 % HNO_3. The lead concentration in these solutions is determined with dithizone by means of a Coleman spectrophotometer.

RESULTS AND DISCUSSION

To calculate the concentration of TEL in the air by means of eqn. 1, the specific
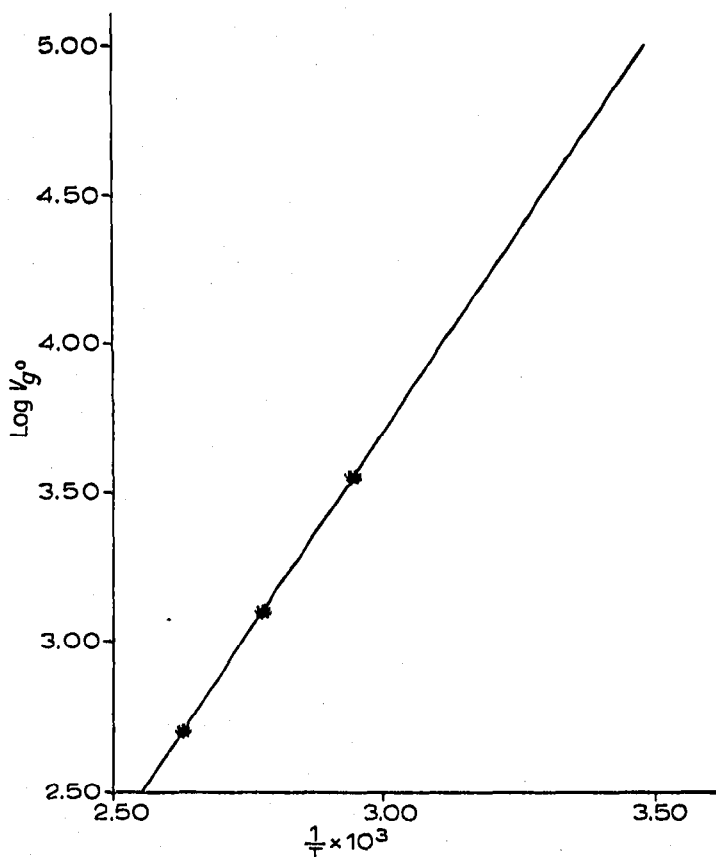

Fig. 4. Plot of log specific retention volumes vs. $1/T$.

TABLE I

DETERMINATION OF TEL AT DIFFERENT DILUTION VALUES OF AIR

Dilution flow rate (ml/min)	Saturation flow rate (ml/min)	Collection temperature (°C)	Calculated concentration (g/ml·10^{10})	Concentration determined by	
				Gas chromatography (g/ml·10^{10})	Spectrophotometry (g/ml·10^{10})
200	6.7	25.0	26.0	25.0	24.2
200	6.7	25.5	26.0	25.5	—
200	4.2	24.5	8.7	8.4	9.1
200	4.2	24.5	8.7	8.9	—
5725	5.0	24.0	6.9	6.5	7.2
5725	5.0	24.0	6.9	7.5	7.2
5200	2.6	0.0	4.1	4.3	4.2
5200	2.6	0.0	4.1	3.9	—
5200	1.0	0.0	1.6	1.9	—
5200	0.9	0.0	1.2	1.0	—
5200	0.9	0.0	1.2	1.1	—

retention volumes at the temperatures of the syringe tube during the sampling procedure should be known.

These data are obtained from a plot of log V_g versus $1/T$ measured at different temperatures of the chromatographic column and extrapolated to lower temperatures. This plot is shown in Fig. 4 and was obtained with an SE-52 column.

To verify the overall procedure a known concentration of TEL in air was prepared with a dynamic dilution apparatus. A slow flow rate of nitrogen saturated with TEL at 0° in a Drechsel type bottle was diluted with a high volume of pure air from a cylinder.

The sampling tube was placed at the exit of the mixing chamber and the air containing a known concentration of TEL was aspirated by suction.

The volume of the gas passed through should be about double the retention volume of TEL in the sampling tube in order to reach the equilibrium state[6].

The concentrations of TEL prepared with different flow rates of saturation and dilution gas and the corresponding values measured by gas chromatographic and spectrophotometric methods are shown in Table I.

The agreement is satisfactory and concentrations down to 10^{-10} g/ml (or 100 p.p.b.) can easily be detected.

MEASUREMENTS IN POLLUTED AIR

The procedure described has been successfully employed for the measurement of the pollution level in the air around a factory where TEL is produced.

Sampling was carried out on different days and in different locations, viz. near the distillation tower, in the plant where the Na–Pb alloy is prepared, and near the furnace where lead is recovered. The results of the analysis for these various places, with their distances from the base of the distillation tower which is the point of maximum pollution, are reported in Table II. These data are compared with the spectrophotometric measurement. As expected the values obtained from the spectrophotometric method are higher than the ones given by the gas chromatographic

TABLE II

DETERMINATION OF TEL IN POLLUTED AIR

Place of sampling	Distance from the distillation tower (m)	Gas chromatographic method (p.p.m.)	Spectrophotometric method (p.p.m.)
Distillation tower	0	0.30	0.37
		0.28	0.28
Na–Pb alloy plant	25	0.31	0.44
		0.29	0.45
Pb scoriae furnaces	40	0.08	0.10
		0.08	0.11
TEL deposit	70	0.05	0.14

procedure. In the spectrophotometric method all the lead in the air in various forms is determined while in gas chromatography only the TEL peak is measured.

This also explains the large differences found between the two procedures for the place where the Na–Pb alloy is prepared.

CONCLUSIONS

Many advantages are offered by this procedure compared with other classical methods. It is specific for alkyl leads, each one giving a peak on the gas chromatogram well resolved from others. The sensitivity is very high using the electron capture detector.

The sampling procedure is extremely simple and many samples can be taken for a determination. It is not necessary to control the amount of air expired and the flow rate. The concentration of TEL in these tubes can be measured later in few minutes with the gas chromatograph.

With this method many chemical manipulations or concentration steps are avoided and the sampling apparatus is very simple and readily portable.

ACKNOWLEDGEMENT

SUMMARY

The concentration of tetraethyllead (TEL) in air near the factories where it is produced can be directly measured by gas chromatography. The method consists in passing the air for analysis through a sampling tube packed with the same material as the chromatographic column. When equilibrium conditions have been established the sample is desorbed and injected into the gas chromatograph. The concentration of TEL is determined from the values of peak areas and the specific retention volumes. The method is simple, rapid and sensitive down to 0.5–0.1 p.p.m.

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