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RAPID DETERMINATION OF LEAD IN USED LUBRICATING OILS ON THIN-LAYER CHROMATOGRAMS

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SUMMARY

Small amounts of lead can be immediately detected on chromatograms (0.2–0.3 μg on cellulose thin layers and about 0.4 μg on paper) as the fluorescent $[PbCl_4]^{2-}$ complex (excitation maximum 254 nm; emission maximum 480 nm). Quantitative determinations can be made by diffuse reflectance measurement at 254 nm. This method was utilized for the determination of lead in used lubricating oils. The analytical range could be extended virtually to the detection limits of fluorescence.

INTRODUCTION

The lead content of lubricating oils, which gradually increases with continued use, must be kept below certain limits for correct engine maintenance. Used lubricating oils may contain suspended particles of lead and lead oxide, together with dissolved breakdown products of tetraethyllead. These oils must therefore be analyzed to determine their lead content on occasions. A sensitive method of detection by fluorescence is available, based on converting all forms of lead to the fluorescent tetrachlorolead complex, which has an emission maximum at 480 nm and an excitation maximum at 254 nm[1]. Lead compounds dissolved in hydrochloric acid will form chloro-complexes according to the reactions

$$PbCl_2 + Cl^- \rightarrow [PbCl_3]^-$$

$$[PbCl_3]^- + Cl^- \rightarrow [PbCl_4]^{2-}$$

and in concentrated hydrochloric acid all of the lead should be bound as the tetrachloro-complex, which is regarded as the fluorescent species. However, excess of chloride ion is expected to quench the fluorescence at room temperature, and the light emission must therefore be observed at either low chloride ion concentration[1], or at low temperature. Belyi and co-workers[2,3] have studied the fluorescence of lead chloride solutions in concentrated hydrochloric acid at low temperature, and have developed a procedure for the fluorimetric determination of trace amounts of lead impurities[4]. As we found this procedure to be rather inconvenient, we attempted to develop an improved method by combining optical and chromatographic techniques. This combination was found to be especially advantageous, as the emission intensity is markedly enhanced when the fluorescent complex is firmly held on a cellulose support[1]. For the quantitative determination of lead, the chromatograms carrying the $[PbCl_4]^{2-}$ complex can be scanned under UV irradiation and the diffuse reflectance intensity recorded. The amount of lead held on the support can be derived from the areas under the recorded peaks or their heights.

This paper describes the utilization of both the detection and the determination of lead admixtures in used lubricating oils. Spectrographic[5] and atomic-absorption[6] methods have been also reported.

MATERIALS AND METHODS

The technique described by Stahl[7] was used for all thin-layer chromatography (TLC) experiments. The chromatographic plates had to be prepared in the laboratory as commercially available cellulose-coated TLC plates exhibited too strong a background fluorescence. A 0.25-mm thickness of microcrystalline cellulose (Merck, Darmstadt, G.F.R.) was applied to 20 × 20 cm glass plates by means of a Desaga (Heidelberg, G.F.R.) spreader. The finished plates were allowed to dry at room temperature, and were re-dried for 10 min at 100° before use. Samples of mineral oil were diluted with xylene–isopropanol (1:1) in order to reduce the viscosity and to bring the expected lead content within the required range. The extent of dilution must, of course, be determined by preliminary experiment. Chromatographic runs were made with internal standards. Equal volumes (4 μl) of lead nitrate solutions, adjusted to contain varying amounts of lead from 0.3 to 5 μg, were first applied to the starting line in the forms of 1-cm-long bands at 1-cm distances, which were dried with hot air and then covered with a fixed volume of diluted sample. The latter was also streaked at the separate origin. The best results were obtained with sample sizes of 2–5 μl. In all instances, the sample and the standard solutions had to be applied in portions, with a pipette having a small cotton wick inserted in its tip, drying with hot air after the application of each portion. The plates were pre-developed with xylene in order to remove excess of oil, then dried.

Development was started with the solvent system[8] acetone–10 *N* hydrochloric acid–water (7:1:2), and was interrupted when the solvent front had travelled a distance of 2 cm from the starting line. The plates were removed from the tank and dried. All forms of lead present in the sample were converted into the desired fluorescent complex during this process. Development was resumed with the same solvent and continued until the solvent front had advanced 10 cm from the start. The developed chromatograms were then thoroughly dried in a stream of hot air. This step is very important because even trace amounts of water or solvent would interfere with the fluorescence.

For the detection of lead, the chromatograms were excited with a low-pressure mercury lamp, through a filter passing the 254-nm band, and the fluorescent spot was located. Quantitative measurements were made by exposing the chromatograms to 254-nm radiation, scanning the spots and recording the diffuse reflectance intensity at the same wavelength. An Opton spectrophotometer with a scanning accessory and an automatic recorder was used for these measurements. The records were evaluated by means of a planimeter or, alternatively, the peak areas were calculated by multiplying the height by the width at half-height. In order to obtain the actual amount of lead in the original samples, the areas were extrapolated graphically[9] to zero internal standard using a least-squares method. The content of lead in the oil was then calculated from the equation

$$\text{Lead, \% (g per 100 ml)} = \frac{X_0}{v} \cdot \frac{V_0 + V_s}{100\, V_0}$$

where X_0 is the amount obtained graphically, v is the volume applied to the starting line, V_0 is the sample volume before dilution and V_s is the volume of the diluent.

Paper chromatography was carried out on Whatman No. 1 paper sheets with the solvent system specified above, under conditions similar to those used for TLC.

RESULTS AND DISCUSSION

The successful separation of lead from other constituents of lubricating oil by TLC is shown by a typical chromatogram in Fig. 1. The spots, located visually following excitation of the fluorophore with 254-nm radiation, had an average R_F value of 0.70.

A faintly fluorescent zone situated near the solvent front appeared on all chromatograms, but did not interfere with the exact location of the lead-carrying spots. It is of interest that no fluorescence was observed in any part of the chromatograms when silica gel was used as the stationary phase.

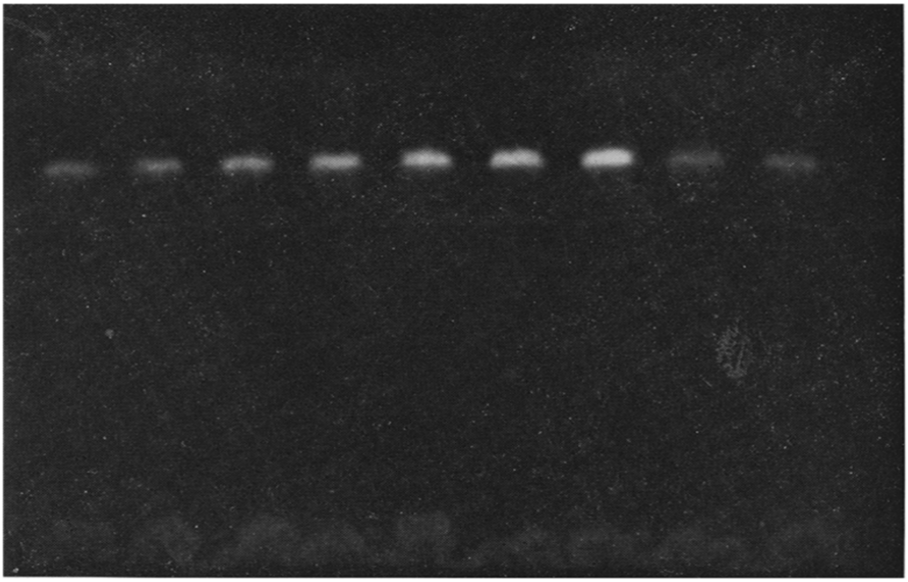

Fig. 1. Separation of lead impurities from other constituents of Delta TLX (SAE 30) lubricating oil. The sample was taken after 23-h use in a Fiat 600D engine and diluted 1 + 1 with xylene–isopropanol (1:1). Sample size, 4 µl. Internal standards: amount of lead added (µg), right to left: 0.3, 0.6, 1.2, 1.8, 2.4, 3.0, 3.6, 0.0, 0.0. Excess of oil was removed by pre-development with xylene. Solvent system, acetone–10 N hydrochloric acid–water (7:1:2). Spots located by excitation at 254 nm.

Amounts as small as 0.2–0.3 μg of lead per spot could be detected with certainty on the thin-layer chromatograms. The detection limit was slightly higher with paper chromatograms, about 0.4 μg of lead being required for definite detection.

Quantitative evaluation of the diffuse reflectance records, of which that in Fig. 2 is representative, gave a linear relationship between the amount of lead present in the spot and the area or height of the corresponding peak (Fig. 3).

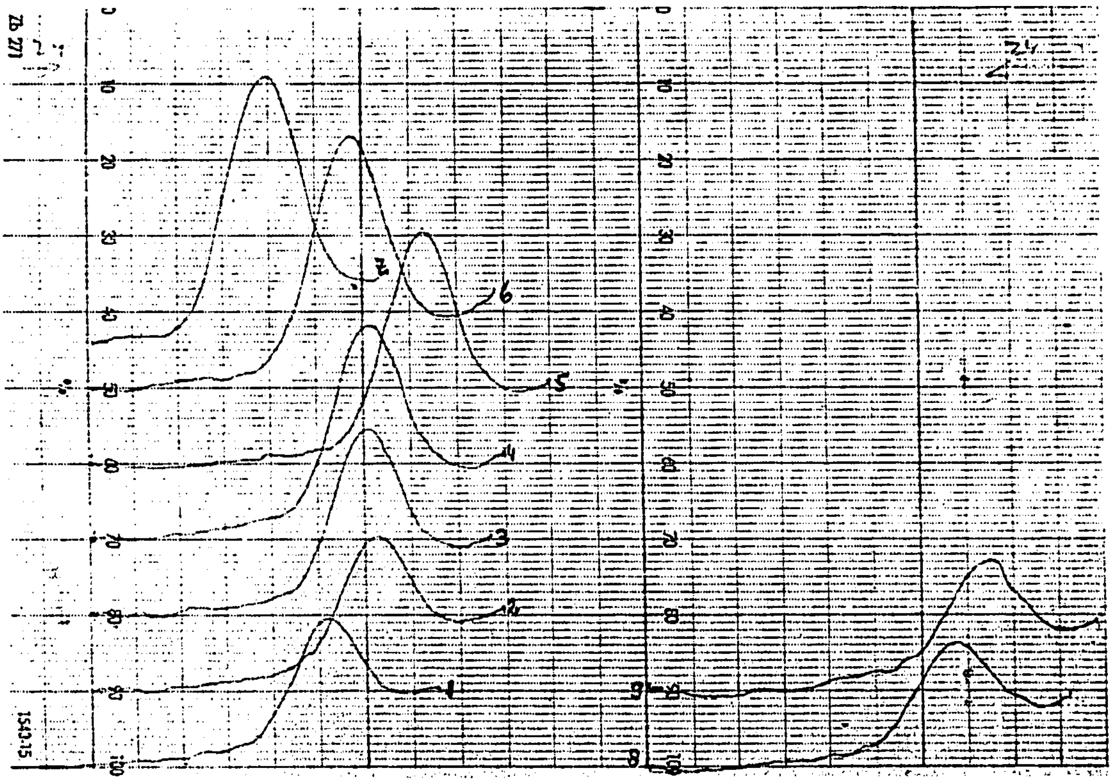

Fig. 2. Diffuse reflectance intensity recording of the chromatogram in Fig. 1, obtained with an Opton Chromatogramm Spektralphotometer unit. Light source, deuterium lamp; exit aperture of illuminating head, 1 × 14 mm; reflected band isolation at 254 nm; scanning speed, 30 mm/min; paper speed in recorder, 120 mm/min.

Table I shows the results obtained in an experiment with samples of Delta TLX (SAE 30) lubricating oil, utilized for various lengths of time in a Fiat 600D engine, and analyzed for increase of lead content at the end of specified test periods.

These results show that the combined method described here for the detection and determination of lead appears to be well adapted to the needs encountered in the analysis of lubricating oils. These specimens may contain various forms of lead, some of which are suspended while others are dissolved, in a mineral oil medium together with components that might possibly interfere. While other methods are usually cumbersome and time consuming, the present method is simple and relatively rapid. It does not require lengthy pre-treatment of samples, except for dilution, and permits

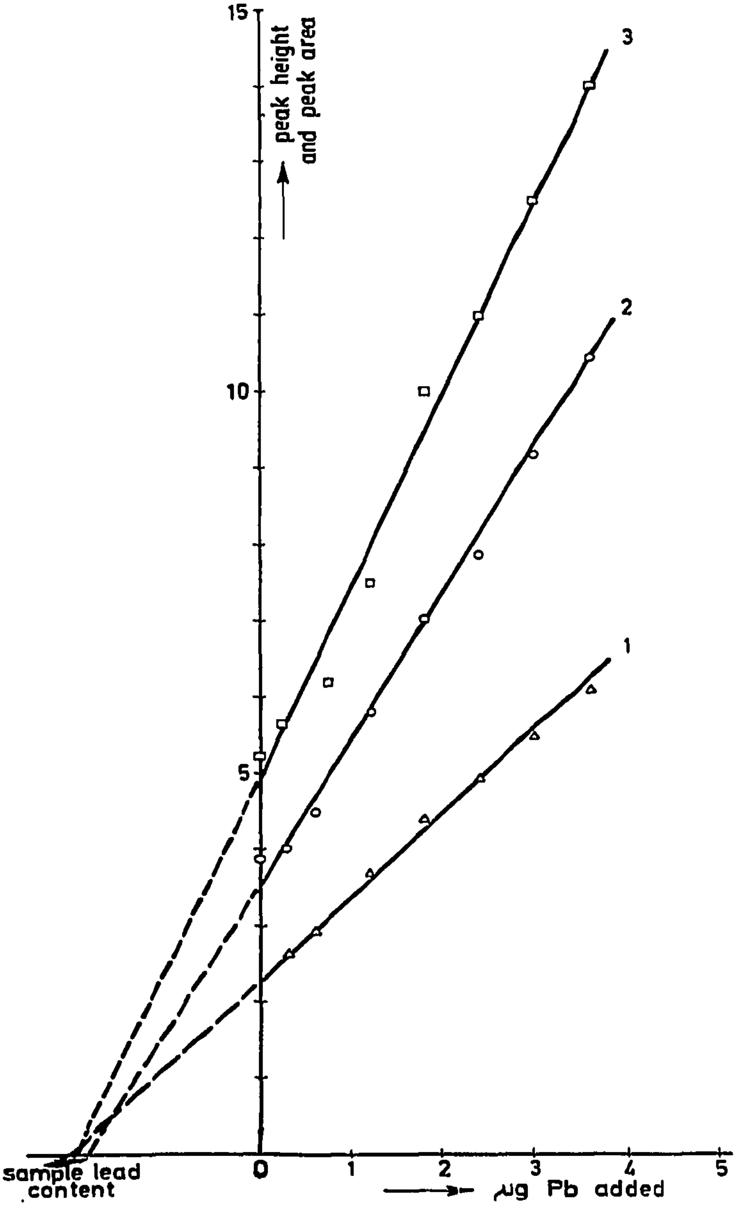

Fig. 3. Relationship between the amounts of lead on spots and (1) the peak height and (2 and 3) areas under the corresponding peaks on diffuse reflectance recordings. Areas were either (2) calculated or (3) determined planimetrically. The line was fitted to the experimental points by the least-squares method.

TABLE I

ACCUMULATION OF LEAD IN DELTA TLX (SAE 30) LUBRICATING OIL UNDER ACTUAL WORKING CONDITIONS IN A FIAT 600D ENGINE

Test period (h)	*Lead content (g/100 ml)*
23	0.100
47	0.308
71	0.381
95	0.460
119	0.419

a clear separation and the concentration of the various forms of lead into a single well defined fraction. The addition of hydrochloric acid to the developing solvent system has the effect not only of bringing the suspended forms of lead into solution, but also of converting these and other forms possibly present in solution *ab initio* into one easily detectable and measurable product. The quantitative determination could, therefore, be carried out immediately, without elution.

As the fluorescence intensity of the final reaction product, $[PbCl_4]^{2-}$, is enhanced by immobilizing the complex in a planar position, the detection is very sensitive, provided that no quenching influence is exercised by the matrix or by interfering substances in sample and reagents. The procedure used in this work effects the removal of such a quencher, the chloride ion, which is eliminated as hydrochloric acid by thoroughly drying the chromatograms in a stream of hot air. Another requirement for maximum sensitivity, namely the reduction of background fluorescence to an insignificant level, was met firstly by avoiding the use of commercial thin-layer plates, and secondly by pre-development with xylene, intended to eliminate water-insoluble, natively fluorescing components of the mineral oil medium. This aim, however, was not achieved completely, as shown by the faintly fluorescent zones that accompanied the solvent front, but these zones were sufficiently far from the spot for the sensitivity of the method not to be impaired. The quantitative results are based on absorption of the 254-nm radiation by the $[PbCl_4]^{2-}$. Such results can be obtained by any type of spectrophotometer equipped with a chromatogram scanning device and recorder, or a combination of such components. Satisfactory linearity between the amount of lead in a spot and the area under the corresponding peak should be easily obtained. Errors should be chiefly those of graphical recording and evaluation.

By applying the above method, the rate of accumulation of lead under actual working conditions was shown to be exceedingly slow during first 50 h, after which it was approximately constant for next 70-h period.

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REFERENCES

1 K. Weber, personal communication.
2 M. U. Belyi and I. J. Rushnipenko, *Izv. Akad. Nauk SSSR, Ser. Fiz.*, 24 (1963) 661.
3 M. U. Belyi and B. F. Rudko, *Ukr. Fiz. Zh.*, 5 (1960) 779.
4 E. A. Bozevalnov and E. H. Solovev, *Zh. Anal. Khim.*, 20 (1965) 330.
5 R. F. Meeker and R. C. Pommati, *Anal. Chem.*, 25 (1953) 70.
6 K. G. Brodie and J. P. Matousek, *Anal. Chem.*, 43 (1973) 1557.
7 E. Stahl, *Dünnschicht chromatographie*, Springer, Berlin, Heidelberg, New York, 1962.
8 I. M. Hais and K. Macek, *Handbuch der Papierchromatographie*, Fischer, Jena, 1958.
9 W. Slavin, *Atomic Absorption Spectroscopy*, Vol. 25, Wiley, New York, 1968, p. 65.