

CHROM. 14,642

PLASMA EMISSION SPECTRAL DETECTION FOR HIGH-RESOLUTION GAS CHROMATOGRAPHIC STUDY OF GROUP IV ORGANOMETALLIC COMPOUNDS

SCOTT A. ESTES, PETER C. UDEN* and RAMON M. BARNES

Department of Chemistry, GRC Towers, University of Massachusetts, Amherst, MA 01003 (U.S.A.)

SUMMARY

Specific element detection for fused-silica capillary column gas chromatography of germanium, tin and lead tetraalkyl organometallics is carried out by means of microwave-induced and sustained helium plasma atomic emission spectroscopy utilizing the TM_{010} cavity. Representative redistribution reactions are monitored and quantitative determinations made of individual products. Different distributions of tetraalkyllead compounds are quantitatively measured in various gasolines.

INTRODUCTION

In any mode of chromatographic separation, when components of interest contain an element not otherwise present in the sample matrix, detection responsive solely to that element gives significant simplification since species containing that element need be resolved only from each other and not from other matrix components.

Atomic emission spectroscopy as a chromatographic detection mode has the inherent advantage of simultaneous multi-element capability with wide dynamic range. The advent of various plasma sources for atomic emission and high-resolution monochromators to minimize spectral interferences has prompted increasing interest in atomic emission chromatographic detection. Microwave-induced and sustained plasmas¹⁻⁵, the argon d.c. plasma^{6,7} and inductively coupled argon plasmas^{8,9} have all been successively employed for gas chromatographic and/or liquid chromatographic applications.

The major advantages of such interfacing are as follows. (a) The ability to perform speciation, with regard to elemental content, either before or within the chromatographic column for many metals and non-metals; application may either be direct or by derivatization. (b) The ability to tolerate non-ideal chromatographic conditions and elution characteristics; incomplete resolution can be tolerated, a factor of great importance in complex matrixes. Elemental selectivity is here a primary concern. (c) The sensitivity of plasma emission detection which in many cases gives detection at or below the pg/sec level. (d) The potential simultaneous multi-element capacity of plasma emission. (e) The compatibility with chromatographic systems by simple interfacing.

In general, plasma emission spectral detection has been much more widely used in gas chromatography than in liquid chromatography, where the many problems associated with solvent background and selectivity still remain to be addressed.

High-resolution gas chromatography (GC) makes heavy demands on detector design, since rapid quantitative response to match capillary column peak dimensions is needed in addition to the usual objectives of optimal detection and wide linear response range. Post-column band broadening must always be minimized, an aim which has been greatly simplified by the advent of flexible inert fused-silica capillary columns which can be routed directly into detection devices with minimal transfer volume. We have reported a detailed study of the characteristics of fused silica and glass capillary column interfaces to the Beenakker TM_{010} resonance cavity^{10,11} for GC-microwave-induced and sustained plasma emission applications^{12,13}. The present paper addresses the application of this system to the specific element detection of redistribution products of alkyl groups on germanium, silicon and lead atoms and to the quantitation of tetraalkyl-lead compounds in gasolines.

The scrambling of alkyl groups on tetraalkyl compounds of Group IVA elements has been studied by various workers^{14,15}. We reported packed-column GC studies on scrambling between pairs of Group IVA elements utilizing the d.c. argon plasma as an element-specific detector¹⁶. Now considered are representative scrambling reactions for mixtures of the type $(R_1)_4M$ and $(R_2)_4M$ where M is germanium, tin or lead and R_1 and R_2 are ethyl, *n*-propyl and *n*-butyl groups. Such reactions yield five redistribution products for each metal center, with quantitative proportions as follows: $(R_1)_4M$, 6.25%, $(R_1)_3R_2M$, 25%, $(R_1)_2(R_2)_2M$, 37.5%, $R_1(R_2)_3M$, 25%, $(R_2)_4M$, 6.25%, assuming equivalent stoichiometric proportions of the starting tetraalkyl compounds.

A partial demonstration of such distributed tetraalkyl organometallic compounds is seen in the various mixtures of tetraethyl-tetramethyl redistributed lead compounds present in different gasolines. Here specific element lead detection serves to resolve these species from the predominant hydrocarbon background.

EXPERIMENTAL

Gas chromatographic systems

Varian 1200 (Walnut Creek, CA, U.S.A.) and Shimadzu Mini-2 (Columbia, MD, U.S.A.) gas chromatographs were used with SP-2100 fused-silica wall-coated open tubular (WCOT) capillary columns (12.5 m \times 0.3 mm O.D. \times 200 μ m I.D.) (Hewlett-Packard, Avondale, PA, U.S.A.). Combination injection port liner splitters were designed for each gas chromatograph, consisting of quartz injection port liners attached to 1/4 in. to 1/16 in. brass Swagelok reducers. The reducers had 1/16 in. holes drilled through their sides into which a piece of 12 in. by 1/16 in. O.D. stainless-steel tubing was silver soldered. A Nupro brass fine-metering valve fitted to the end of the stainless-steel tubing served to adjust the injection split ratio.

Details of the spectrometer (Heath 703, McPherson Instruments, Acton, MA, U.S.A.), microwave power train and interface have been published elsewhere¹². In the study described herein, the fused-silica capillary column was passed through a heated interface without any end-column splitting and terminated within 1–5 mm of the external wall of the Beenakker TM_{010} microwave cavity (Fig. 1). An alternative

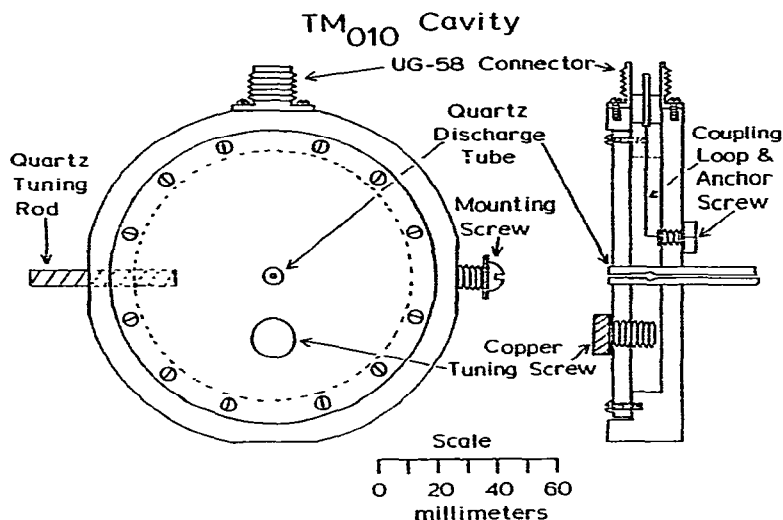


Fig. 1. Diagram of the TM_{010} cylindrical resonance cavity used to sustain the atmospheric pressure helium plasma.

system allowing for solvent venting and/or effluent splitting was described in detail^{1,2}. The essentials of the TM_{010} microwave cavity configuration are shown in Fig. 1.

Materials

Tetra-*n*-propyltin, tetraethyltin, tetraethylgermanium, tetra-*n*-butylgermanium, and tetra-*n*-butyllead were obtained from Ventron Corporation (Beverly, MA, U.S.A.). Tetraethyllead was obtained from ROC/RIC Chemical Corporation (Sun Valley, CA, U.S.A.) and gasoline samples were purchased from local retail stations. Helium carrier gas and plasma gas was purified by passage through anhydrous calcium chloride and molecular sieve 3A traps.

Operational parameters

The operational parameters of the GC-microwave plasma emission system are given in Table I.

Redistribution reaction procedure

A total volume of 100 μ l of liquid sample mixtures was placed in a 2-ml screw-capped glass vial. A 5–10-mg piece of resublimed anhydrous aluminum chloride was added and the vial immediately closed with an aluminum foil lined screw-cap. The vial was placed on a hot plate at 100–120°C, its top being cooled by a forced air draft from a hood to prevent rupture while under reflux. After 30 min, heating was stopped and the product liquid diluted with hexanes. Dilution ratios were adjusted (between 20:1 and 100:1) to give chromatographic peaks containing from 1 ng to 10 ng for microbore fused-silica capillary column analysis.

RESULTS AND DISCUSSION

The redistribution of representative examples of the mixture type $(R_1)_4M$ and

TABLE I
GC-MED OPERATING PARAMETERS

<i>Chromatographic</i>				
Column	SP-2100 WCOT			
packing	Fused silica (Carbowax pretreated)			
material	12.5 m × 300 μm O.D. × 200 μm I.D.			
dimensions				
Injection				
split	100:1 110:1			
volume	0.10 μl			
Carrier gas flow-rate (helium)	1 ml/min			
Temperatures				
column program	40°C to 140°C at 5°C/min and 80°C to 134°C, 176°C or 186°C at 6°C/min			
injector	210°C to 215°C			
transfer block	170°C to 220°C			
inter:face oven	160°C to 220°C			
<i>Spectroscopic</i>				
Entrance and exit slit				
width	25 μm			
height	12 mm			
PMT tube and voltage	RCA 1P28. 700 V			
Recorder	1.0 V full scale input, 1.0 cm/min			
Picoammeter time constant	0.10 sec			
Element	C(I)	Ge(I)	Sn(I)	Pb(I)
Wavelength observed nanometers	247.86	265.16	284.0	283.3
Total plasma flow-rate.				
helium (ml/min)	70	341	341	100
Microwave input power	75	58	58	75
Picoammeter gain (A)				
5 V full scale output	3 · 10 ⁻⁶	3 · 10 ⁻⁷	1 · 10 ⁻⁶	1 · 10 ⁻⁷
Hydrogen doping				
0.5-1.0 ml/min	no	yes	yes	yes

(R₂)₄M is shown in Figs. 2, 3 and 4 for the compound pairs tetraethyl- and tetra-*n*-butylgermanium, tetraethyl- and tetra-*n*-propyltin and tetraethyl- and tetra-*n*-butyllead, respectively. For each of the product mixtures it is seen that qualitative re-distribution of alkyl groups had occurred. The sensitivity of the Beenakker TM₀₁₀ microwave detector towards germanium, tin and lead is evident from the elemental detection levels for individual compounds indicated in the chromatograms. Quantitation for the starting compounds was by peak area measurement calibration, while that for intermediate compounds was by interpolation with an accuracy estimated at ± 3% relative. The absence of observed solvent response and background indicates the high selectivities of these elements over carbon under the conditions employed.

In Table II are shown the detection limits, selectivities and linear dynamic ranges of response for the three elements. All detection limits are in the low or sub picogram range with selectivities over carbon in the region of 100,000.

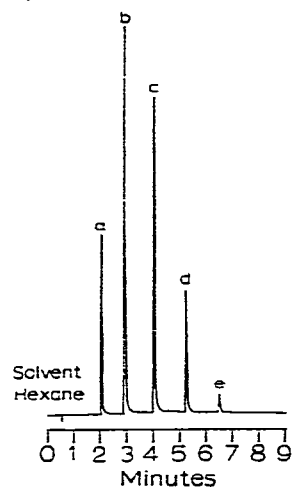
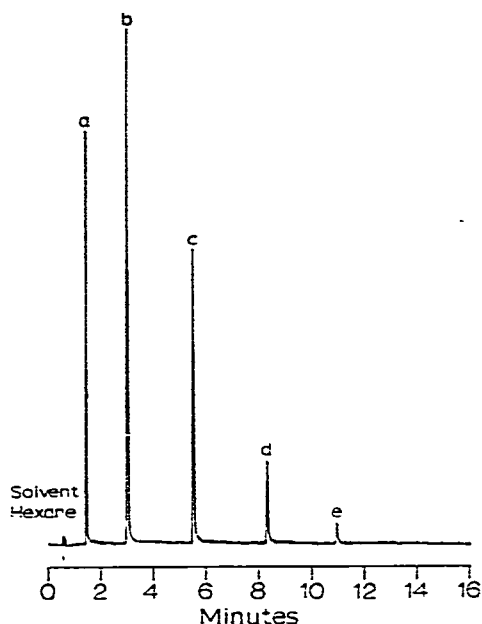


Fig. 2. Gas chromatogram of the alkyl redistribution products between tetraethylgermanium and tetra-*n*-butylgermanium. The microwave emission detector (MED) monitoring Ge(I) 265.16 nm. Column 12.5 m SP-2100 WCOT fused-silica capillary. Temperature program from 80 at 6°C/min. Injection 0.10 μ l, split 110:1. Peaks: a = $(\text{CH}_3\text{CH}_2)_2\text{Ge}$, 494 pg Ge; b = $(\text{CH}_3\text{CH}_2)_3(n\text{-CH}_3\text{CH}_2\text{CH}_2\text{CH}_2)\text{Ge}$, 722 pg Ge; c = $(\text{CH}_3\text{CH}_2)_2(n\text{-CH}_3\text{CH}_2\text{CH}_2\text{CH}_2)_2\text{Ge}$, 509 pg Ge; d = $(\text{CH}_3\text{CH}_2)(n\text{-CH}_3\text{CH}_2\text{CH}_2\text{CH}_2)_3\text{Ge}$, 145 pg. Ge; e = $(n\text{-CH}_3\text{CH}_2\text{CH}_2\text{CH}_2)_4\text{Ge}$, 32 pg Ge. Hydrogen bleed 0.5–1 ml/min.

Fig. 3. Gas chromatogram of alkyl redistribution products between tetraethyltin and tetra-*n*-propyltin. MED at Sn(I) 284.00 nm; column and conditions as in Fig. 2, except temperature program from 80 to 134°C at 6°C/min and split 100:1. Peaks: a = $(\text{CH}_3\text{CH}_2)_4\text{Sn}$, 0.78 ng Sn; b = $(\text{CH}_3\text{CH}_2)_3(n\text{-CH}_3\text{CH}_2\text{CH}_2\text{CH}_2)\text{Sn}$, 2.17 ng Sn; c = $(\text{CH}_3\text{CH}_2)_2(n\text{-CH}_3\text{CH}_2\text{CH}_2)_2\text{Sn}$, 2.70 ng Sn; d = $(\text{CH}_3\text{CH}_2)(n\text{-CH}_3\text{CH}_2\text{CH}_2)_3\text{Sn}$, 0.82 ng Sn; e = $(n\text{-CH}_3\text{CH}_2\text{CH}_2)_4\text{Sn}$, 0.12 ng Sn.

Quantitative theoretical and attained redistribution of the mixtures is given in Table III, the data indicating that each mixture has moved towards the theoretical extent of rearrangement but has not attained it. Examination of the absolute levels of each element measured in the chromatograms, taking into account an initial dilution of 100:1, an injection volume of 0.10 μ l and an injection split of 100:1 or 110:1, indicates that for lead and germanium a considerable amount of the element is not longer present as tetraalkyl species after reaction. In all cases 5–10 ng of metal should be present in the cumulative peak total for each redistribution chromatogram. The tin redistribution approaches this criterion and is the only chromatogram where an approach is seen to theoretical and quantitative scrambling.

The loss of tetraalkyllead compounds through chlorination by the aluminum chloride has been observed¹⁶; a larger, less polar alkyl group should be more easily replaced with a chloride, than would be a smaller, more polar alkyl group. Hence chlorination should be to the disadvantage of butyl groups in the redistribution, as is seen in the calculated molar ratio of 2.14 seen for ethyl to butyl groups as eluting. The loss of germanium, although less evident than for the lead system is clearly apparent.

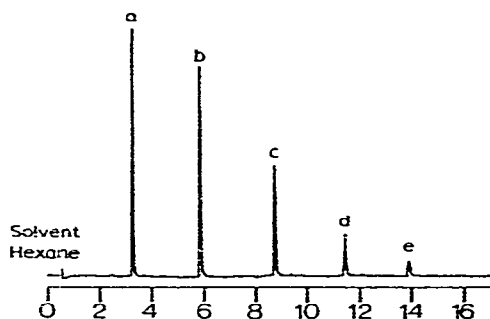


Fig. 4. Gas chromatogram of the alkyl redistribution products between tetraethyllead and tetra-*n*-butyllead. MED at Pb(I) 283.3 nm; column and conditions as in Fig. 2, except temperature program from 80 to 182°C at 6°C/min and split 100:1. Peaks: a = $(\text{CH}_3\text{CH}_2)_4 \text{Pb}$, 180 pg Pb; b = $(\text{CH}_3\text{CH}_2)_3(n\text{-CH}_2\text{CH}_2\text{CH}_2\text{CH}_2) \text{Pb}$, 189 pg Pb; c = $(\text{CH}_3\text{CH}_2)_2(n\text{-CH}_2\text{CH}_2\text{CH}_2\text{CH}_2)_2 \text{Pb}$, 162 pg Pb; d = $(\text{CH}_3\text{CH}_2)(n\text{-CH}_2\text{-CH}_2\text{CH}_2\text{CH}_2)_3 \text{Pb}$, 62 pg Pb; e = $(n\text{-CH}_2\text{CH}_2\text{CH}_2\text{CH}_2)_4 \text{Pb}$, 21 pg Pb.

Although possibly attributable to chlorination, some decomposition may give rise to the unidentified rust-colored precipitate observed in this reaction. Again a higher proportion of butyl groups is no longer present as tetraalkyls, as is seen from the ethyl:butyl molar ratio of 2.28. Ethyl substituents are more strongly covalently bound to germanium than butyl groups.

The employment of hydrogen doping of the helium plasma to improve the characteristics of elements such as germanium, tin and lead has been reported earlier¹³. In general it doubles or triples the elemental signal for hydride-forming elements such as boron, aluminium, germanium, tin, lead, phosphorus and arsenic and is absolutely necessary for the GC-microwave emission analysis of volatile boron compounds¹⁷. The addition of hydrogen to the helium discharge also improves the ability of the plasma to resist "overload" by germanium, tin and lead at throughput rates of more than 1–2 ng/sec in the plasma. The "overload" is defined as that amount of mass flow-rate of element which causes metal to deposit on the discharge tube walls. The deposited element, which rests on the walls of the tube immediately after the hottest portion of the discharge, slowly vaporizes off causing the tailing which can be noticed in Fig. 3 for tin compounds and slightly in Fig. 2 for the largest peaks of germanium. In Fig. 4, overloading is not seen for lead compounds since levels are well below the overload condition.

TABLE II
DETECTION LIMITS, SELECTIVITIES AND LINEAR DYNAMIC RANGES

<i>Element and emission wavelength (nm)</i>	<i>Absolute detection limits (pg)</i>	<i>Detection limit (pg/sec)</i>	<i>Selectivity vs. C</i>	<i>Linear dynamic range</i>
Ge(I) 265.1	3.9	1.3	$7.57 \cdot 10^4$	10^3
Sn(I) 284.0	6.1	1.6	$3.58 \cdot 10^5$	10^3
Pb(I) 283.3	0.71	0.17	$2.46 \cdot 10^5$	10^3

TABLE III

CALCULATED AND EXPERIMENTAL VALUES FOR THE PROPORTIONS OF REDISTRIBUTION PRODUCTS FROM FRIEDEL-CRAFTS CATALYZED REACTIONS

Reaction (A): tetraethylgermanium and tetra-*n*-butylgermanium. Reaction (B): tetraethyltin and tetra-*n*-propyltin. Reaction (C): tetraethyllead and tetra-*n*-butyllead.

Compound	$(R_1)_4M$	$(R_1)_3R_2M$	$(R_1)_2(R_2)_2M$	$R_1(R_2)_3M$	$(R_2)_4M$
Theoretical (%)	6.25	25.00	37.50	25.00	6.25
<i>Reaction A</i>					
Germanium alkyls	Et ₄ Ge	Et ₃ Bu ⁿ Ge	Et ₂ Bu ₂ ⁿ Ge	EtBu ₃ ⁿ Ge	Bu ₄ ⁿ Ge
Experimental (%)	26.0	37.9	26.7	7.6	1.7
Ethyl:butyl molar ratio = 2.28					
<i>Reaction B</i>					
Tin alkyls	Et ₄ Sn	Et ₃ Pr ⁿ Sn	Et ₂ Pr ₂ ⁿ Sn	EtPr ₃ ⁿ Sn	Pr ₄ ⁿ Sn
Experimental (%)	13.0	36.2	35.2	13.7	2.0
Ethyl:propyl molar ratio = 1.51					
<i>Reaction C</i>					
Lead alkyls	Et ₄ Pb	Et ₃ Bu ⁿ Pb	Et ₂ Bu ₂ ⁿ Pb	EtBu ₃ ⁿ Pb	Bu ₄ ⁿ Pb
Experimental (%)	29.3	30.7	26.4	10.2	3.4
Ethyl:butyl molar ratio = 2.14					

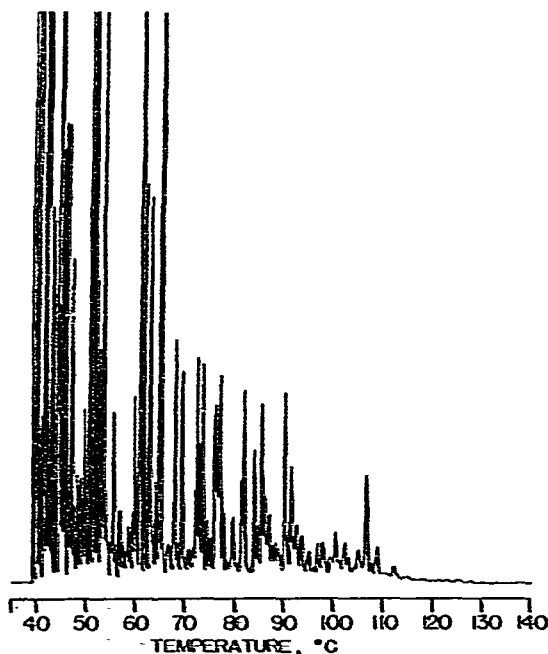


Fig. 5. Gas chromatogram of Super Shell leaded gasoline. MED at C(I) 247.86 nm. Column as in Fig. 2. Temperature program from 40 to 140°C at 5°C/min. Injection 0.10 μ l, split 100:1.

Characterization of tetraalkylleads in leaded gasoline

The high complexity of gasoline is seen in the fused-silica capillary chromatogram shown in Fig. 5, where the microwave plasma detector is set to the 247.9 nm (C(I) emission line and is used similarly to a flame ionization detector to acquire a total organic compound assessment of a mixture. Leaded gasolines contain different alkylleads, typically the methyl-/ethyllead redistribution mixture. Figs. 6 and 7 depict gasoline tetraalkyllead profiles, monitoring the 283.3 nm Pb(I) emission line. Chromatographic separation and spectral resolution of lead over carbon background are well demonstrated. Patterns showed reproducibility of greater than 2.5% relative standard deviation. Super Shell and Amoco gasolines contain mixed methyl-/ethylleads in differing proportions, while Exxon contains primarily tetraethyllead with some triethyllead chloride also present¹². The microwave plasma emission system is clearly applicable to such gasoline characterizations, similar applications having been demonstrated by other workers with GC-plasma¹⁸ and GC-atomic absorption analysis¹⁹.

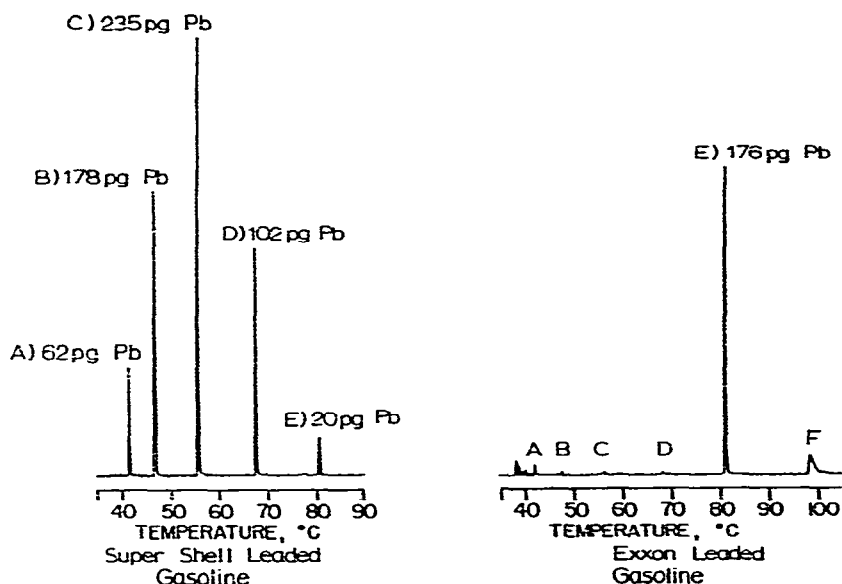


Fig. 6. Gas chromatograms of Super Shell and Exxon leaded gasolines. MED at Pb(I) 283.3 nm; column and conditions as in Fig. 5, except temperature program from 40 to 100°C at 5°C/min. Peaks: A = $(\text{CH}_3)_4\text{Pb}$; B = $(\text{CH}_3)_3(\text{CH}_3\text{CH}_2)\text{Pb}$; C = $(\text{CH}_3)_2(\text{CH}_3\text{CH}_2)_2\text{Pb}$; D = $(\text{CH}_3)(\text{CH}_3\text{CH}_2)_3\text{Pb}$; E = $(\text{CH}_3\text{CH}_2)_4\text{Pb}$; F = $(\text{CH}_3\text{CH}_2)_3\text{PbCl}$.

ACKNOWLEDGEMENTS

This work was supported in part by the Ethyl Corporation, Ferndale, MI, U.S.A., by the U.S. Department of Energy through contract DE-AC02-077EV4320, and by a National Institutes Biomedical Sciences Research Grant to the University of Massachusetts. We also thank Bruce D. Quimby and the Hewlett-Packard Corporation, Avondale, PA, U.S.A. for provision of the fused-silica capillary column. We

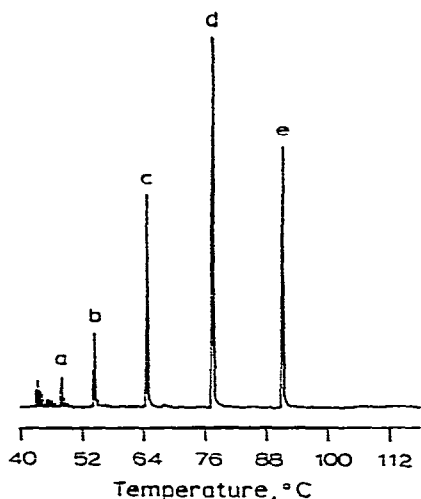


Fig. 7. Gas chromatogram of Amoco leaded gasoline. Detector, column and conditions as in Fig. 5. Gain $3 \cdot 10^{-7}$ A. Peaks: a = $(\text{CH}_3)_4 \text{Pb}$, 10 pg Pb; b = $(\text{CH}_3)_3 (\text{CH}_3\text{CH}_2) \text{Pb}$, 30 pg Pb; c = $(\text{CH}_3)_2 (\text{CH}_3\text{CH}_2)_2 \text{Pb}$, 96 pg Pb; d = $(\text{CH}_3) (\text{CH}_3\text{CH}_2)_3 \text{Pb}$, 169 pg Pb; e = $(\text{CH}_3\text{CH}_2)_4 \text{Pb}$, 131 pg Pb.

thank the American Chemical Society, Analytical Division for provision of Fellowship Support (SEA) awarded by the Proctor and Gamble Company, Cincinnati, OH, U.S.A.

REFERENCES

- 1 A. J. McCormack, S. C. Tong and W. D. Cooke, *Anal. Chem.*, 37 (1965) 1470.
- 2 W. R. McLean, D. L. Stanton and G. E. Penketh, *Analyst (London)*, 98 (1973) 432.
- 3 B. D. Quimby, P. C. Uden and R. M. Barnes, *Anal. Chem.*, 50 (1978) 2112.
- 4 B. D. Quimby, M. F. Delaney, P. C. Uden and R. M. Barnes, *Anal. Chem.*, 51 (1979) 875.
- 5 K. J. Mulligan, J. A. Caruso and F. L. Fricke, *Analyst (London)*, 105 (1980) 1060.
- 6 R. J. Lloyd, R. M. Barnes, P. C. Uden and W. G. Elliott, *Anal. Chem.*, 50 (1978) 2025.
- 7 P. C. Uden, R. M. Barnes and F. P. DiSanzo, *Anal. Chem.*, 50 (1978) 852.
- 8 D. Sommer and K. Ohls, *Z. Anal. Chem.*, 295 (1979) 337.
- 9 D. L. Windsor and M. B. Denton, *J. Chromatogr. Sci.*, 17 (1979) 492.
- 10 C. I. M. Beenakker, *Spectrochim Acta*, 31B (1976) 483.
- 11 C. I. M. Beenakker, *Spectrochim Acta*, 32B (1977) 173.
- 12 S. A. Estes, P. C. Uden and R. M. Barnes, *Anal. Chem.*, 53 (1981) 1336.
- 13 S. A. Estes, P. C. Uden and R. M. Barnes, *Anal. Chem.*, 53 (1981) 1829.
- 14 G. Calingaert and H. A. Beatty, *J. Amer. Chem. Soc.*, 61 (1939) 2748.
- 15 F. Pollard, G. Nickless and P. C. Uden, *J. Chromatogr.*, 19 (1965) 28.
- 16 S. A. Estes, C. A. Poirier, P. C. Uden and R. M. Barnes, *J. Chromatogr.*, 196 (1980) 265.
- 17 L. G. Sarto, Jr., S. A. Estes, P. C. Uden, S. Siggia and R. M. Barnes, *Anal. Lett.*, 14(A3) (1981) 205.
- 18 D. C. Reamer, W. H. Zoller and T. C. O'Haver, *Anal. Chem.*, 50 (1978) 1449.
- 19 J. C. van Loon, *Amer. Lab.*, 13(5) (1981) 47.