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ELEMENTAL MICROANALYSIS OF ORGANIC AND ORGANOMETALLIC COMPOUNDS USING PYROLYSIS-GAS CHROMATOGRAPHY

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SUMMARY

The multielemental microanalysis of organic and organometallic compounds using pyrolysis-gas chromatography is described. Samples are pyrolyzed in a hydrogen-helium atmosphere at a high temperature and the elements converted to the corresponding hydride by means of a catalyst. Separation and analysis of the hydride mixture is performed using a gas chromatograph equipped with a flame ionization detector. Another portion of the pyrolysate is passed over a catalyst and assayed using a gas chromatograph equipped with a thermal conductivity detector. Up to nine elements (carbon, oxygen, nitrogen, sulfur, phosphorus, silicon, bromine, iodine or chlorine) may be assayed simultaneously using this system for compounds of molecular weight up to 300 g per mole.

INTRODUCTION

The development of analytical methods for elemental microanalysis has progressed significantly since their initial development in the early twentieth century. The individual analysis of many elements can now be performed on a routine basis using these classical techniques. Simultaneous elemental microanalysis has also developed rapidly since the initial investigations of Pregl *et al.* Current commercial instrumentation is capable of the simultaneous analysis of three elements (for example carbon, hydrogen and nitrogen) by either oxidative or reductive combustion**.

The analysis of the Group IVA through VIA elements has classically been treated on an individual basis with separation of two elements necessary prior to the finish of the analysis. Hydride generation techniques using various detector systems have been employed for several elements¹, but again, the number of elements and the elements, themselves, have been limited in previous methods of analysis.

The current report describes a system for the simultaneous analysis of up to

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** E.g., Perkin-Elmer Model 240C elemental analyzer (Perkin-Elmer, Norwalk, CT, U.S.A.), and Carlo Erba Model 1106 elemental analyzer (Carlo Erba, Milan, Italy).

nine elements in a sample by means of reductive combustion followed by dual gas chromatographic analysis.

EXPERIMENTAL

Equipment and apparatus

The apparatus used in this work has been previously described² with several modifications. It includes a microcombustion train containing an ignitor, microcombustion furnace and Vycor combustion tube for static pyrolysis of the sample. A tee connection was installed directly downstream of the combustion train. After combustion, one half of the pyrolysate is passed through heated transfer tubing directly into a gas chromatograph equipped with a flame ionization detector. The other half is passed through heated transfer lines, across a catalyst and into a gas chromatograph equipped with a thermal conductivity detector.

The carrier gas system was composed of helium and hydrogen gases which were proportioned by means of calibrated rotameters. In normal operation the helium:hydrogen ratio was set at 80:20. This ratio allowed sufficient hydrogen to enter the combustion tube during pyrolysis while minimizing the safety hazard of excess hydrogen in the laboratory.

The thermal conductivity detection (TCD) unit which was used has been described previously³. It consisted of a dedicated Perkin-Elmer 154D gas chromatograph that had been re-designed for dual column operation. The chromatographic

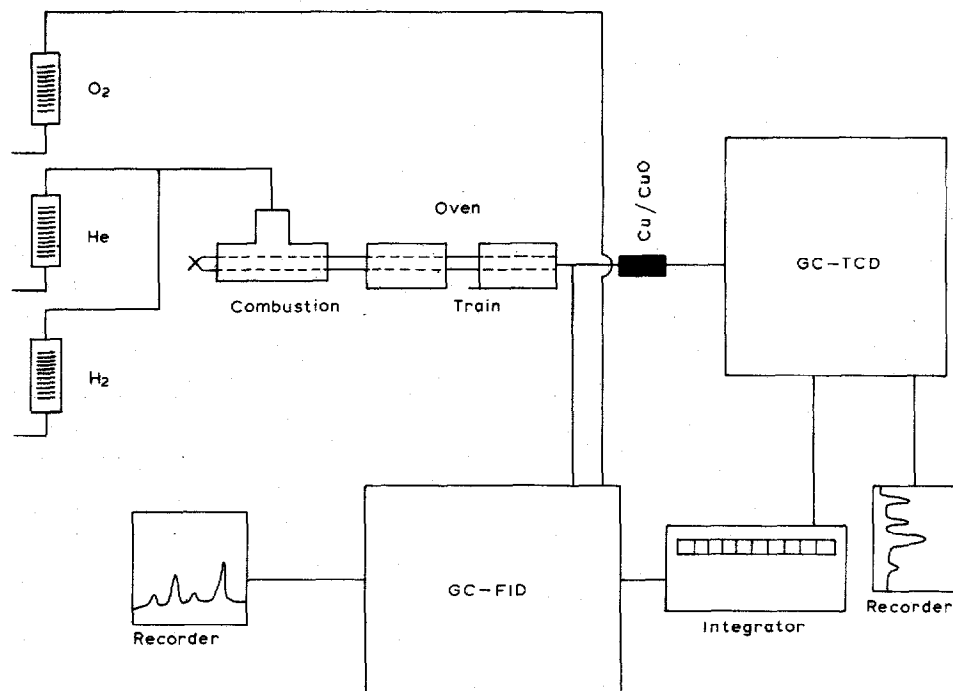


Fig. 1. Instrumentation schematic for elemental micro-analysis of organic compounds using pyrolysis-gas chromatography.

columns and the detector are aligned in a series-across-detector (SAD) mode in which the combustion products first pass through one chromatographic column and then through one side of the thermal conductivity detector. The products then pass through a second chromatographic column and through the second side of the detector. This arrangement allows for the separation of all of the products of combustion in a reasonable length of time. Any gas chromatograph equipped with a thermal conductivity detector is suitable for this type of work with the appropriate modifications for SAD alignment.

The flame ionization detection (FID) unit used was a dedicated Perkin-Elmer F-11 chromatograph. This instrument was fitted for single-column (or dual-column in series) use. Oxygen was used as the support gas rather than breathing air in order to increase the response of the unit to hydrogen sulfide. Fig. 1 shows a schematic flow diagram of the system used in this work (any gas chromatograph with some capabilities may be used in this system).

Catalysts

In order to convert the combustion products to the appropriate species for analysis, several catalysts were employed at various points in the system. Magnesium powder was added to each sample capsule to facilitate the reduction process during combustion. Nickel was impregnated on glass wool by dissolving nickel nitrate in water, soaking glass wool in the solution, then evaporating the water. A 5-cm length of this nickel-impregnated glass wool was placed just downstream of the ignitor in the combustion tube and the combustion furnace was heated to 400°C in an oxygen atmosphere. The nickel nitrate was thus converted to nickel oxide⁴. After several hours, the carrier was changed to helium and the nickel oxide was reduced to nickel. The catalyst temperature was then reduced to 350°C and maintained by means of the second stage of the combustion furnace. Nickel was found to completely convert carbon to its hydride (methane) in the presence of hydrogen. Similar results were found for phosphorus (PH₃), silicon (SiH₄), sulfur (H₂S) and nitrogen (NH₃).

Copper-copper oxide catalyst was used for the conversion of ammonia to molecular nitrogen. About 10 cm of the copper-copper oxide mixture was placed in a 1/4 in. stainless steel tube just upstream of the thermal conductivity detector and maintained at 200°C during the analysis (see Fig. 1).

Reagents and samples

Preparation of gas standards and synthetic gas mixture has been previously described². Mixtures of gases were prepared in helium for calibration of the system and for measurement of retention times. Infrared spectra were obtained for both pure gases and combustion products for the confirmation of the identity of the combustion products.

All samples used were reagent grade and were dried in a desiccator over Drierite prior to use.

Pyrolysis optimization

Pyrolysis of organic and organometallic compounds in the presence of helium results in the formation of various fragment molecules. Depending upon the nature of the original compound, the molecular weight and volatility of the fragments, a

fingerprint pyrogram may be obtained when gas chromatography is used to assay the pyrolysate. This fingerprint is useful in characterizing certain families of compounds and specific components can sometimes be measured for quantitative analysis.

It was the aim of this work to pyrolyze certain compounds to the extent that specific low-molecular-weight volatile compounds would result which would be representative of the elemental composition of the original compound. The initial combustion of compounds containing some of the nine elements in question yielded a whole range of pyrolysate components. Optimization of combustion time, temperature and carrier gas was undertaken to limit each element to a specific pyrolysis product.

It was found that combustion in an atmosphere of helium-hydrogen (80:20) for 1 min over a nickel catalyst at 650°C would yield products which were suitable for gas chromatographic multielemental analysis. Combustion of compounds containing the nine elements under study yielded the products shown in Table I.

After combustion, these products were passed into the two gas chromatographs for separation and analysis. The components to be quantified using FID were methane (CH_4), phosphine (PH_3), silane (SiH_4) and hydrogen sulfide (H_2S). The other compounds either do not respond to the flame or do not interfere with the analysis.

Chromatographic separation and quantification could not be achieved for the nine elements with TCD, so a copper-copper oxide catalyst was placed in line, upstream of the detector and maintained at 200°C. At this temperature, methane, water and the halogens (Br_2 , HCl , I_2) were not affected by the catalyst. Phosphine, silane and hydrogen sulfide did not elute and were probably trapped on the catalyst. Ammonia was converted to molecular nitrogen quantitatively. Thus, the species to be separated with the thermal conductivity detector were methane, water, bromine, iodine, hydrogen chloride and nitrogen.

Chromatographic separation

The initial trials for the hydride separation were performed on a 4 ft. \times 1/8 in. PTFE column packed with Caropak B-HT. The separation for methane and

TABLE I
COMBUSTION PRODUCTS OBTAINED UNDER OPTIMIZED PYROLYSIS CONDITIONS

<i>Element</i>	<i>Combustion product</i>
C	CH_4
P	PH_3
Si	SiH_4
S	H_2S
Br	Br_2
I	I_2
Cl	Cl_2
O	H_2O
N	NH_3

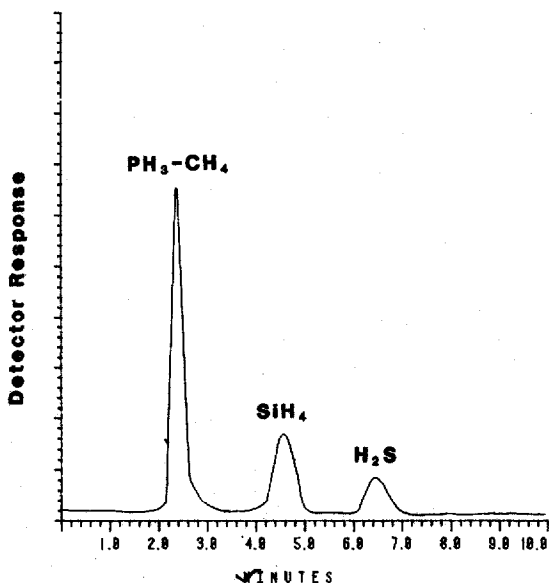


Fig. 2. FID chromatogram of a mixture of reagent methane, phosphine, silane and hydrogen sulfide.

silane was adequate; however hydrogen sulfide and phosphine were not separated from the methane peak. The addition of a 4 ft. \times 1/8 in. PTFE column packed with Chromosorb 102 succeeded in the separation of hydrogen sulfide from methane. By coupling these two columns in series, the required separation could be performed. Methane and phosphine could not be separated using this system. The oven door of the gas chromatograph was left open during the analysis which allowed the column temperature to equilibrate at 30°C. A typical chromatogram obtained using this system is shown in Fig. 2.

For the TCD separation, hydrogen chloride and molecular bromine and iodine had previously been separated using a 3 ft. \times 1/4 in. 20% SE-30 on Chromosorb W-AW (60-80 mesh) column². The resolution of these compounds on this column proved to be more than adequate. The second column used in the SAD mode was an 8 ft. \times 1/8 in. PTFE column packed with Carbosieve S (100-120 mesh). This column proved to be adequate for the separation of methane, molecular nitrogen and water. Samples of pure gases were injected onto the column at 90°C and the separation of all six components was achieved with these two columns.

Fig. 3 shows the chromatogram obtained from the injection of pure combustion product gases at 90°C with a hydrogen-helium flow-rate of 20 ml/min for the two columns aligned in the SAD mode.

Combustion of a number of compounds containing the various elements to be determined was then performed to check the operation of the system. Quantification was possible for carbon (as methane), oxygen (as water), silicon (as silane), sulfur (as hydrogen sulfide), nitrogen, chlorine (as hydrogen chloride), and bromide and iodine. As phosphine could not be separated from methane in the FID mode, its concentration was determined by the difference between the phosphine-methane peak in the FID mode and the methane peak in the TCD mode. Combustion product confir-

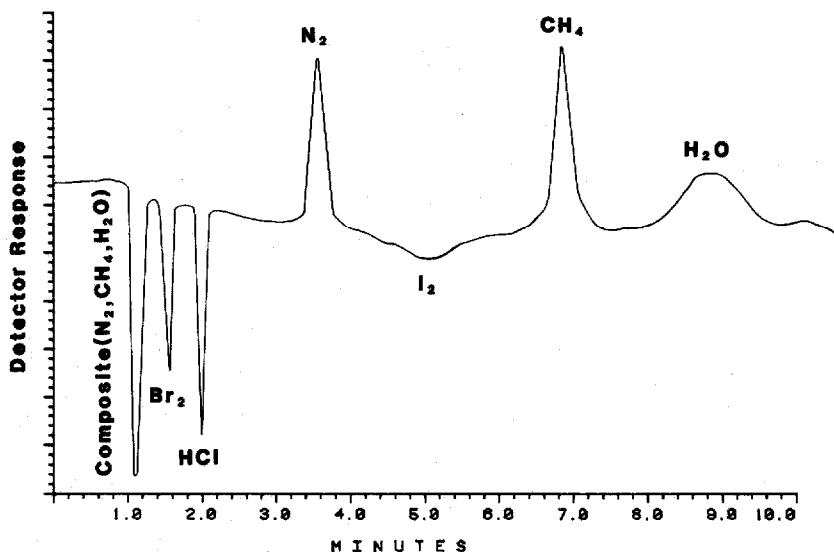


Fig. 3. TCD chromatogram of a mixture of reagent methane, nitrogen, water, hydrogen chloride, bromine and iodine after separation in the SAD mode.

mation was performed using gas-phase infrared and wet chemical techniques and by comparison of retention times of the combustion products to those of known standards.

Typical analysis

A typical analysis using this system is performed as follows. A 1.000-mg (± 0.001 mg) sample is weighed into an aluminum sample capsule. Liquid samples are transferred into a capsule with a syringe. The capsules for liquid samples are pre-filled with *ca.* 50 mg of magnesium powder to adsorb the liquid sample. Solid samples are then covered with *ca.* 50 mg of the magnesium powder. The capsules are then crimped, sealed and stored in a desiccator until they are to be used.

The micro-combustion ovens are heated to 650 and 350°C, respectively, and the heated transfer tubing to 110°C. The copper-copper oxide catalyst oven was heated to 200°C and the thermal conductivity detector oven heated to 90°C. The flame ionization detector oven door was left open to equilibrate at room temperature (30°C).

The sample capsule is placed on the tip of the ignitor, which is then sealed into the Swagelok tee with the stainless steel nut. The hydrogen-helium carrier gas is then passed over the sample at 20 ml/min (5 min) to remove oxygen from the system, and then the carrier flow is interrupted by means of the bypass valves. The d.c. charge is then applied to the ignitor for 1 min as pyrolysis takes place. After pyrolysis, the carrier flow is resumed (hydrogen-helium) and the d.c. charge is disconnected from the ignitor. The combustion ovens are then moved away from the combustion tube.

After 2.5 min, a signal is seen for methane-phosphine on the flame ionization detector recorder. This peak is followed by those for ethane and hydrogen sulfide. The composite peak consisting of methane, nitrogen and water is seen on the thermal

TABLE II

EXPERIMENTAL RESULTS

Theoretical percentages shown in parentheses. Allowable error for classical micro-analysis: C, ± 0.3 ; O, ± 0.3 ; N, ± 0.2 ; S, ± 0.3 ; P, ± 0.3 ; Si, ± 0.2 ; X, $\pm 0.3\%$.

Compound	Sample weight, mg	C (%)	O (%)	N,S (%)	P,Si (%)	X (%)
<i>p</i> -Aminophenol	1.402	66.10 (66.04)	14.70 (14.66)	12.61 (12.83)		
	1.008	66.01	14.77	13.01		
	0.786	65.83	14.92	13.15		
	0.911	66.16	14.61	12.70		
	0.988	66.33	14.72	13.19		
	0.952	66.24	15.00	12.44		
	Mean	66.11	14.79	12.85		
	Std. Dev.	0.18	0.15	0.31		
<i>tert.</i> -Butyldimethylchlorosilane	1.304	47.72 (47.81)			18.82 (18.63)	23.49 (23.52)
	1.116	48.01			18.60	23.66
	0.941	47.94			18.42	23.60
	1.169	47.59			18.47	23.32
	0.835	47.86			18.79	23.55
	1.250	47.91			18.70	23.29
	Mean	47.84			18.63	23.49
	Std. Dev.	0.16			0.17	0.15
Chloroacetic acid	1.891	25.66 (25.42)	33.34 (33.86)			37.76 (37.52)
	0.675	25.51	33.66			37.36
	0.864	25.77	33.94			37.68
	0.917	25.61	34.04			37.41
	1.141	25.28	33.85			37.18
	1.102	25.48	33.98			38.28
	Mean	25.55	33.80			37.61
	Std. Dev.	0.17	0.26			0.39
<i>p</i> -Chloroaniline	1.290	56.35 (56.49)		11.25 (10.98)		27.59 (27.79)
	1.006	56.53		11.33		28.18
	0.869	56.37		11.06		27.65
	0.990	56.09		11.19		27.57
	1.105	56.50		11.20		27.81
	0.941	56.68		10.73		28.02
	Mean	56.42		11.13		27.80
	Std. Dev.	0.20		0.21		0.25
Dithiooxamide	0.774	20.16 (19.99)		53.55 (53.35)-S		
				23.78 (23.31)-N		
	0.992	19.91		53.38		
				23.40		
	1.141	20.12		52.97		
				23.06		
	0.861	20.39		53.38		
				23.46		
	0.891	20.41		53.19		
				23.59		
1.301	19.79		53.51			
			23.23			
Mean	20.13		53.33-S	23.42-N		
Std. Dev.	0.25		0.22	0.26		

(Continued on p. 226)

TABLE II (continued)

Compound	Sample weight, mg	C (%)	O (%)	N,S (%)	P,Si (%)	X (%)
Triethylphosphite	0.765	43.48 (43.37)	29.02 (28.89)		18.85 (18.64)	
	1.246	43.58	29.12		19.16	
	1.219	43.35	28.74		18.47	
	0.847	42.78	28.60		18.78	
	1.002	43.18	29.18		18.68	
	1.194	43.56	28.92		19.01	
	Mean	43.32	28.93		18.83	
	Std. Dev.	0.30	0.22		0.24	
N,O-bis(trimethylsilyl)-acetamide	0.816	45.90 (45.76)	12.01 (12.19)	10.58 (10.67)	21.48 (21.40)	
	1.226	46.01	12.34	10.50	21.38	
	1.041	45.75	12.13	10.72	21.23	
	1.220	45.80	12.39	10.62	21.52	
	0.974	45.57	12.16	10.87	21.68	
	0.861	45.68	12.27	10.78	21.25	
	Mean	45.79	12.22	10.68	21.42	
	Std. Dev.	0.17	0.14	0.14	0.17	
Triphenylphosphine oxide	0.793	77.42 (77.69)	5.68 (5.75)		11.44 (11.13)	
	0.839	77.23	5.77		11.53	
	1.304	77.42	5.94		11.08	
	0.911	77.13	5.55		11.22	
	1.187	77.78	5.41		10.98	
	0.845	77.06	5.56		11.31	
	Mean	77.34	5.65		11.26	
	Std. Dev.	0.26	0.19		0.21	
Trimethylchlorosilane	1.021	33.23 (33.17)			25.65 (25.85)	32.46 (32.63)
	0.896	33.31			25.52	32.73
	1.173	33.15			25.58	32.82
	1.309	32.90			25.82	32.59
	1.155	33.33			25.90	32.71
	0.944	33.25			25.80	32.52
	Mean	33.20			25.71	32.64
	Std. Dev.	0.16			0.25	0.14

conductivity detector recorder after 1 min. This is followed by the peaks for the six components separated in the SAD mode. Calculations are based on peak areas as reported by the digital integrator.

RESULTS

Having determined that all of the compounds to be tested were relatively pure, a series of analyses were performed to test the limits of the system. Twenty compounds were assayed for carbon, oxygen, silicon, phosphorus, sulfur, nitrogen, chlorine, bromine and iodine. Each element in a compound was assayed a minimum of

six times. Selected data for these analyses are reported in Table II. The data obtained for these analyses show that all analyses for all compounds were within 2% relative standard deviation.

Twelve compounds were also assayed using a double blind technique. Each compound was identified by number and by the elements to be assayed in that particular compound. The results obtained in these analyses were within 3% relative deviation of the theoretical percentage for each element.

CONCLUSIONS

The initial design of this project proposed to explore the possibility of the simultaneous microanalysis of certain elements in organic and organometallic compounds using several combustion-chromatographic techniques. The system described above is one in which nine elements (carbon, phosphorus, oxygen, sulfur, silicon, nitrogen, chlorine, bromine and iodine) may be determined simultaneously. Several more elemental determinations may be performed per run than had previously been possible.

There are two potential limitations of this system. First, compounds of high molecular weight may fail to combust completely thus yielding low results and, secondly, compounds containing a high oxygen content may form carbon monoxide if sufficient hydrogen is not present at the time of combustion. This may cause low results for both carbon and oxygen in a particular sample. Using a different ratio of helium to hydrogen will correct the problem.

REFERENCES

- 1 G. Guiochon and C. Pommier, *Gas Chromatography in Inorganics and Organometallics*, Ann Arbor Science, Ann Arbor, 1973.
- 2 J. F. Sullivan, R. L. Grob and P. W. Rulon, *J. Chromatogr.*, 261 (1983) 265.
- 3 R. L. Grob and P. W. Rulon, *Chem. Instr.*, 6 (1975) 87.
- 4 H. W. Lang, *Standard Method No. 29*, Bureau of Mines, U.S. Department of the Interior, 1972.