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MULTIELEMENTAL MICROANALYSIS OF ORGANIC COMPOUNDS USING GAS CHROMATOGRAPHY

J. F. SULLIVAN*, R. L. GROB* and P. W. RULON**

Department of Chemistry, Villanova University, Villanova, PA (U.S.A.)

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SUMMARY

Multielemental microanalysis of organic compounds has been performed using oxidative combustion and gas chromatographic separation and quantitation. Samples of low-molecular-weight compounds (less than 300 g/mol) are combusted at a high temperature in a pure oxygen atmosphere. The combustion products are then passed directly into a gas chromatograph for separation and detection. Using this system the elements carbon, hydrogen, sulfur, chlorine, bromine and iodine may be assayed with an average absolute deviation of 0.5 %. Nitrogen may be assayed separately by passing the combustion products over a catalyst and converting the nitrogen oxides, formed during combustion, to molecular nitrogen. In this manner the nitrogen content of organic compounds may be determined with an average absolute deviation of 0.4 %.

INTRODUCTION

Elemental microanalysis using gas chromatography (GC) has been performed previously[1-8], but the number of elements assayed in a single sample has been limited. Commercial instrumentation is now limited to the analysis of three elements per sample and five elements overall.

The current work is capable of the analysis of up to six elements (carbon, hydrogen, sulfur, chlorine, bromine or iodine) simultaneously, and seven elements overall. The process involves oxidative combustion followed by GC separation and detection using two chromatographic columns in the series-across-detector (SAD) alignment.

EXPERIMENTAL

Equipment and apparatus

The instrumentation consists of a combustion system and a modified gas chro-

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* Present address: Arco Chemical Company, Newtown Square, PA, U.S.A.
** Present address: Norwich Pharmaceutical Company, Norwich, CT, U.S.A.

matograph equipped with a thermal conductivity detector (TCD). The combustion system consists of an ignitor, a combustion tube and a two-stage microcombustion furnace. The ignitor is prepared by silver soldering a 2-in. section of Nichrome wire (0.04 in., 18 gauge (Ga) alloy type A between two 8 × 0.06 in. (16 Ga) pieces of copper wire (end to end). This soldered piece of wire, composed of three components, is then folded in half, and a 3-mm section of Pyrex glass tubing is slipped over one end to insure electrical insulation. The two ends of the wire are then pushed through a neoprene septum until the ends extend about 2 in. on the other side. The bent Nichrome end of the wire is then placed into a 3/8-in. union tee and sealed with a 3/8-in. Swagelok nut. Copper wire is used in combination with the Nichrome wire rather than a single section of Nichrome wire because of the higher electrical conductivity of copper. Thus, the copper wire remains cool while the Nichrome tip of the ignitor glows red. The neoprene septum permits the direct injection of gases and liquids into the combustion tube without disassembling the ignitor.

Power to the ignitor is supplied via a standard 30-A direct current (d.c.) line available in the laboratory. A 9-V power supply was found to be sufficient to cause the Nichrome tip of the ignitor to glow red without causing excessive heating of the copper wire leeads.

The combustion tube is composed of a 9 mm × 45 cm section of Vycor tubing. Vycor has been proven to be quite satisfactory as a combustion tube in that its physical strength, cost and availability are superior to either quartz or Pyrex. Both 6-mm and 9-mm diameter tubing were found to perform equally well during the combustion of organic compounds, though the 9-mm tubing was found to be easier to work with because of the larger internal area available in which to place the ignitor system and the sample capsule.

A plug of Pyrex wool is positioned in the combustion tube approximately 2.5 cm (1 in.) downstream of the sample. Pyrex wool is added to trap any carbon fog that is formed during the combustion. The carbon is converted to carbon dioxide before it becomes deposited on the walls of the combustion tube.

One end of the combustion tube is sealed into a 3/8-in. Swagelok union with a graphite ferrule and a 3/8-in. nut. The ignitor is placed into the other end of the union tee and sealed into the combustion tube. Carrier gas (oxygen) is passed into the combustion tube through the third opening in the tee. Bypass valves are located behind and in front of the combustion tube so that carrier gas can be diverted from the combustion tube and still be delivered to the gas chromatograph.

The two-stage microcombustion furnace (No. 5679A, von Czoernig-Alber) was available from A. H. Thomas (Philadelphia, PA, U.S.A.) but it is no longer commercially available. However, any heating unit capable of maintaining temperatures up to 750°C may be used to heat the combustion zone. The first stage (20.2 × 7.0 × 6.4 cm) was used to volatilize the sample. The second stage (20.3 × 7.0 × 6.4 cm) was used to maintain the sample at a high temperature to permit complete oxidation of the sample. The maximum temperature of the 3-A furnace was rated at 750°C.

The overall design of the combustion system is shown in Fig. 1.

The gas chromatograph used was a Perkin-Elmer, Model 154D, that had been modified and reequipped for dual column operation[9]. Any gas chromatograph with dual thermal conductivity detectors capable of having two columns connected in-series-across the detector can be used.
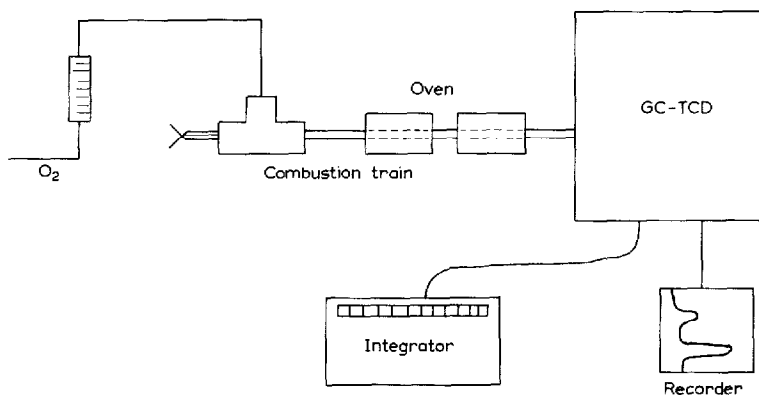
Fig. 1. Drawing of instrument design for multielement microanalysis of organic compounds using GC.

As in classical oxidative combustion, oxygen is used as the carrier gas in this system. The oxygen passes from the cylinder through a drying tube, a molecular sieve trap and then through a calibrated rotameter into the combustion tube. The carrier is then transferred through heated aluminum tubing to the gas chromatograph.

The combustion gas is suitable for the complete oxidation of most samples attempted. The thermal conductivity detector had been equipped with glass-bead thermistors in place of the usual filaments in order to prevent burnout of the detector in an oxygen atmosphere. No significant loss of sensitivity was observed in the detector with the use of glass-bead thermistors.

The balance used for weighing the samples was a Mettler, Model 5A, capable of weighing up to 10 g with an accuracy of ± 0.001 mg. The balance was kept in a thermostated, constant humidity balance room to minimize the error in sample weights.

Reagents, samples and columns

Samples used in this research were obtained from a variety of sources. All samples were the highest purity available and were used as received except that all were dried in a vacuum desiccator over indicating Drierite for at least 24 h prior to use.

Gas standards. Pure gas standards were obtained from the Matheson Gas Lyndhurst, NJ, U.S.A.). In order to measure the retention time of each combustion product, sample of the gas was injected into a 500-ml gas sample bulb equipped with a septum (Cat. No. 7011 and 7016; Alltech, Deerfield, IL, U.S.A.). Concentrations of each standard gas were prepared separately in order to give a peak height of about 60 % of full scale recorder response.

The bulb was first flushed with oxygen, then partially evacuated. The standard gases were then added with a gas-tight syringe, bringing the bulb to atmospheric pressure, and mixed with a magnetic stirring bar. Mixtures of gases were prepared in a similar manner to confirm the separation obtained with a particular chromatographic column. Samples of these mixtures were also used for the measurement of retention times in the confirmation of combustion product identity. For combustion products that are solids (I_2) or liquids (Br_2) at room temperature, the sample bulbs were heated to above room temperature to volatilize the component prior to use.

Oxidation catalysts. Some samples proved to be difficult to combust. This was demonstrated by the deposition of carbon on the inside walls of the combustion tube and by the low results obtained for several elements. To avoid this situation, va-

nadium pentoxide (V_2O_5) was added as a contact-oxidation catalyst to insure complete oxidation of the sample compound. As it was difficult to predict which samples would require the oxidation catalyst, V_2O_5 was added to each sample. In this manner the variable of the presence or absence of the catalyst was eliminated.

Elements typically assayed. Elements typically assayed by direct oxidation include carbon, hydrogen, sulfur, chlorine, bromine and iodine. When combusted, these elements are converted to the corresponding oxidation products for GC separation and quantitation.

Carbon, hydrogen, bromine and iodine all form specific combustion products quantitatively. Chlorine may form either hydrogen chloride or molecular chlorine, depending upon the relative ratio of hydrogen to chlorine in the compound and the temperature at which combustion occurs. For most instances, hydrogen chloride is the preferred form of chlorine for detection. Molecular chlorine was assayed only when sufficient hydrogen was not present to form hydrogen chloride quantitatively.

Nitrogen forms mixed oxides when combusted in an oxygen atmosphere. Since several species result from the combustion of a nitrogen-containing compound, it is not possible to quantitate the concentration of nitrogen in a compound using direct oxidation.

Sulfur in an organic compound may form either sulfur dioxide or sulfur trioxide when combusted. It has been found that sulfur dioxide is the predominant species formed at combustion temperatures less than 650°C. Both species are found at temperatures greater than 650°C. By controlling the combustion temperature at 625°C, sulfur dioxide can be measured quantitatively.

Column selection. Two chromatographic columns were used for the separation of the oxidation products. A 3 ft. × 1/4 in. glass column packed with 20 % SE-30 on Chromosorb W AW (60–80 mesh) was used for the separation of chlorine, bromine and iodine. This column, however, showed an adjusted retention time of zero for carbon dioxide, sulfur dioxide and water; all three compounds elute as a single peak.

A 6 ft. × 1/4 in. glass column of Chromosorb 102 (60–80 mesh) was used for the separation of carbon dioxide, sulfur dioxide and water. Hydrogen chloride and molecular bromine and iodine, however, exhibit excessively long retention times on this column. The retention of these halogens does not affect the separation efficiency of this column. The column is restored to its original condition by heating to 225°C overnight.

Using the series-across-detector (SAD) mode, the components may be separated using the two chromatographic columns described above. In the SAD mode, the combustion products pass through the first chromatographic column (20 % SE-30 on Chromosorb W AW) and then through one side of the thermal conductivity detector. The components then pass through the second column (Chromosorb 102) and through the second side of the detector. In this manner all six components may be separated and quantitated. Fig. 2 shows the separation obtained for a mixture of standard gases using the SAD technique.

Product confirmation

In order to confirm the identity of the compounds formed during direct oxidation, several chemical and instrumental techniques were performed.

Wet chemical analysis. The presence of hydrogen chloride or molecular chlorine was confirmed by passing the products of the combustion of an organo-
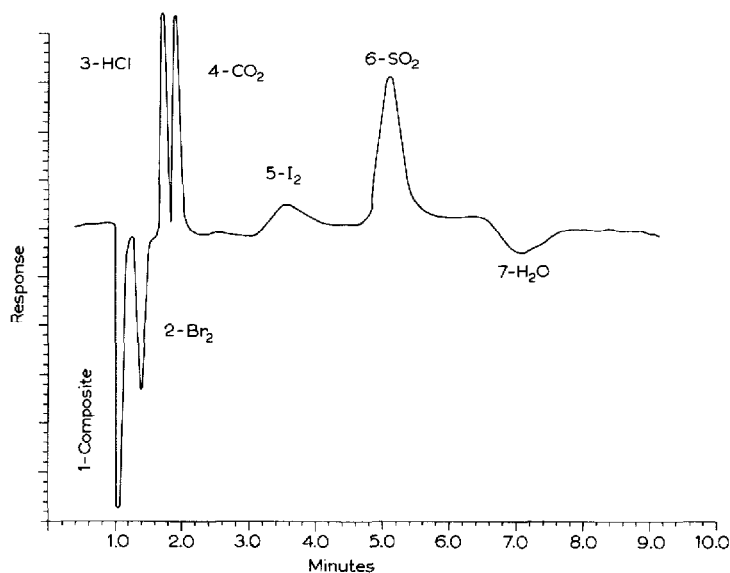
Fig. 2. Typical chromatogram showing the separation of the six elements as combustion products using the instrument design shown in Fig. 1. Peaks shown are inverted due to change in polarity switch.

chlorine compound into a 0.1 M solution of silver nitrate. The predicted presence of hydrogen chloride was confirmed by the formation of a white precipitate of silver chloride. No precipitate was found for molecular chlorine.

Organobromine and organoiodine compounds were similarly combusted and the combustion products were passed in to a 0.1 M silver nitrate solutions. No precipitate was observed for either bromine or iodine, indicating that the predicted forms of molecular bromine and iodine were present as the combustion products.

The presence of bromine and iodine was also confirmed by passing the combustion products of organobromine and organoiodine compounds into carbon tetrachloride. The occurrence of a yellow-orange color for bromine or a purple color for iodine confirmed the presence of bromine or iodine as combustion products.

Retention time. The retention times of all combustion products were measured and compared with those of gas standards injected under similar chromatographic conditions. In all cases the retention times of the combustion product were the same as those of the gas standards.

Instrumental techniques. Gas-phase infrared analysis was performed on all combustion products as another confirmatory technique. The apparatus consists of an 8 cm $\times$ 4 mm glass test-tube with a side arm for trapping the products, a container of liquid nitrogen and a 10-cm gas-phase infrared cell with sodium chloride windows.

For each analysis, the product was trapped in the glass test-tube as it passed out of the thermal conductivity detector and out to the atmosphere. For chlorine, bromine and iodine, the second column (Chromosorb 102) was removed from the instrument and replaced with a blank glass column to prevent the sample from being trapped on the column.

As the product passed through the detector, the glass test-tube was attached to the exit tubing of the detector with a short length of 1/8-in. diameter Tygon tubing. The test-tube was then placed into liquid nitrogen. After the product of interest was trapped, the tubing was removed from the exit of the detector.

For products that are liquids (Br_2) at liquid nitrogen temperature ($-196°C$), a syringe was inserted into the test-tube to remove the product and inject it into the

TABLE I

EXPERIMENTAL RESULTS: OXIDATIVE COMBUSTION

Values in parentheses are the theoretical percentages.

Compound	Sample weight (mg)	%C	%H	%S	%X
Oxalic acid	1.112	26.45 (26.68)	2.08 (2.24)		
	0.975	26.82	1.96		
Dimethylglyoxime	0.849	41.71 (41.37)	7.11 (7.96)		
	0.936	41.46	6.94		
Chloroacetic acid	1.091	25.55 (25.42)	3.11 (3.21)		37.77 (37.51)
	1.163	25.70	2.96		37.37
1-Bromo-4-iodobenzene	0.834	25.21 (25.47)	1.57 (1.43)		27.99 Bromine (28.25)
	1.075	25.01	1.71		27.90
					44.80 Iodine (44.86)
					44.96
Dithiooxamide	1.204	19.76 (19.98)	3.53 (3.36)	52.97 (53.34)	
	1.192	19.64	3.32	53.63	
4-Ethyl-3-thiosemicarbazide	1.406	30.07 (30.23)	7.37 (7.63)	27.16 (26.90)	
	1.128	30.27	7.54	26.76	
Iodobenzene	0.802	35.58 (35.32)			62.34 (62.20)
	1.103	35.69			62.01
Phenol	0.989	76.69 (76.57)	6.69 (6.44)		
	1.216	76.43	6.43		

infrared cell that had previously been flushed with oxygen. For solid products (I_2) the test-tube was connected directly to the infrared cell that had previously been flushed with oxygen and partially evacuated. The test-tube trap was then warmed to convert the product to the gas phase and to pass it into the infrared cell. Several repetitions of this procedure were usually necessary for solid products in order to achieve a high enough concentration of the compound in the infrared cell to confirm the product form.

Infrared analysis was performed for the confirmation of carbon (CO_2), sulfur (SO_2), chlorine, bromine and iodine using this system. As expected, no infrared spectra were observed for bromine or iodine or for the combustion products trapped for bromine and iodine. Infrared spectra for CO_2, SO_2 and HCl trapped after combustion matched those of pure standards, thus confirming these species as combustion products.

Nitrogen analysis

Since nitrogen forms a mixture of oxides when combusted in oxygen, it was necessary to convert these oxides to a single product before chromatographic analysis.

The combustion products exiting the combustion tube were trapped in a molecular sieve 5A trap which was immersed in liquid nitrogen and the carrier gas was changed from oxygen to helium. After the oxygen was purged from the system the trap was warmed to room temperature and the combustion products were passed across a copper–copper oxide catalyst at 540°C where the oxides of nitrogen were converted to molecular nitrogen. The nitrogen thus generated was then passed into the gas chromatograph for separation from the other products and quantitation.

Typical analysis

A typical analysis for a compound containing carbon, hydrogen, sulfur, bromine or iodine would be performed in the following manner.

Approximately 1 ± 0.001 mg of sample is weighed into a 0.05-ml aluminum sample capsule. Approximately 50 mg of vanadium pentoxide catalyst are then added to cover the sample. The ends of the capsule are then crimped closed and the capsule is stored in a desiccator until the analysis is performed.

The first stage of the two-stage combustion furnace is heated to 700°C, the second stage to 625°C and the transfer tubing to 110°C. The 154-D gas chromatograph oven is heated to about 90°C, the injection port to 120°C and the thermal conductivity detector to 110°C. The carrier bypass valves are switched to remove the combustion tube from the carrier gas line and the ignitor is removed. The aluminum sample capsule is placed on the Nichrome tip of the copper–Nichrome ignitor wire. The ignitor is replaced in the combustion tube and the Swagelok nut is tightened to prevent leaks. The carrier bypass valves are then switched back to allow oxygen to pass over the sample.

After about 1 min, the d.c. power is applied to the ignitor and the two stages of the combustion furnace are moved over the combustion tube; combustion then takes place. Combustion of the sample is evidenced by a flash within the combustion tube. After one more minute has elapsed, the d.c. power is disconnected from the copper leads of the ignitor, and the two stages of the combustion furnace are pushed back away from the combustion tube.

The gaseous combustion products exit from the combustion tube in a plug and travel through the heated transfer tubing to the gas chromatograph. The first peak

observed on the recorder (after 1 min) is due to the combined carbon dioxide, sulfur dioxide and water. This initial peak in followed by peaks for bromine, hydrogen chloride, carbon dioxide, iodine, sulfur dioxide and water. Both positive and negative peaks are observed because oxygen is used as the carrier gas. Calibration is performed by comparison of peak areas of each element from a standard (reference) compound to the peak areas of each element in the unknown compound.

A typical chromatogram depicting the separation of the six combustion products is shown in Fig. 2.

RESULTS

Sixteen organic compounds were assayed in duplicate using the direct oxidation system described above. A total of 86 analyses were performed for the simultaneous determination of carbon, hydrogen, sulfur, chlorine, bromine or iodine. Of the results reported, all values fall within 0.5 % absolute deviation of the theoretical value. Several of these results are reported in Table I.

Seven compounds were assayed for nitrogen using the modified combustion and the copper–copper oxide catalyst. The values reported for nitrogen are within 0.4 % absolute deviation of the theoretical value. Data obtained from these nitrogen analyses are shown in Table II.

TABLE II

NITROGEN ANALYSIS

Compound	Sample weight (mg)	% Found	% Theory	Absolute deviation (%)
Glycine	1.020	Standard	18.66	
Glutamic acid	1.047	9.36	9.52	0.16
Piperazine	1.138	32.20	32.53	0.33
p-Nitroaniline	0.672	20.01	20.29	0.28
1,1-Diphenylhydrazine	1.137	14.92	15.21	0.29
Acetamide	1.054	23.41	23.72	0.31
Urea	0.820	47.03	46.65	0.38

CONCLUSIONS

The apparatus described provides a rapid means for the simultaneous analysis of several elements in an organic compound. This system has been used with much success for complex samples containing a wide range of functional groups.

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