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AEC RESEARCH AND DEVELOPMENT REPORT

THE MICRO-DETERMINATION OF CARBON, HYDROGEN, AND NITROGEN IN ORGANIC AND ORGANOMETALLIC COMPOUNDS

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ABSTRACT

Carbon, hydrogen, and nitrogen in a variety of unusual organic and organometallic compounds were determined accurately and precisely with a commercial instrument consisting of a high temperature combustion furnace coupled with a gas chromatograph and equipped for automatic operation.

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INTRODUCTION

Elemental analyses for carbon, hydrogen, and nitrogen are required for assigning or confirming the chemical structures of organic and organometallic compounds synthesized in various programs at the Savannah River Laboratory. New organic extractants are being sought for the improved separation of actinides, lanthanides, and fission products. Organometallic compounds are being synthesized in a broad study of their structure.

The most generally applicable and most reliable methods for carbon, hydrogen, and nitrogen assay employ high temperature dry oxidation of the compound to produce gaseous products that can be measured quantitatively. In the conventional Pregl method[1] for carbon and hydrogen assay, the sample is oxidized at ~900°C with a metal oxide. The oxidation products are swept by oxygen into previously weighed adsorption traps in which the CO_2 and H_2O products are selectively collected and weighed. Nitrogen is usually determined by the Dumas method[1] in which the sample is oxidized and the nitrogen oxides produced are reduced to N_2. The N_2 is determined volumetrically after collection over aqueous caustic.

Takeuchi and Mori[2] examined statistically many of the factors influencing the precision and accuracy of one of the earlier automatic instruments for the analysis of carbon, hydrogen, and nitrogen, the F & M Model 180 C-H-N Analyzer.* Francis[3] reviewed the performance of several such instruments. In general, these early commercial analyzers suffered from mechanical difficulties and lack of precision, and were not widely applicable to many types of organic compounds. This report describes Savannah River Laboratory experience in the analysis of unusual organic and organometallic compounds with an improved C-H-N analyzer.

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* Product of F & M Scientific Corp., Division of Hewlett-Packard Co.

SUMMARY

Carbon, hydrogen, and nitrogen in a variety of unusual organic and organometallic compounds were determined accurately and precisely with a C-H-N analyzer. The instrument consists primarily of a high temperature combustion furnace coupled with a gas chromatograph, and is largely automated. Each determination takes only eight minutes, using preweighed samples of only 0.6 to 0.7 mg.

The precision and accuracy of the automated analyses are equivalent to that obtained by the classical methods, and are not adversely affected by the presence of oxygen, phosphorus, sulfur, chlorine, fluorine, and metals in the samples. The precisions (relative standard deviations) for carbon, hydrogen, and nitrogen determinations are 0.6, 1.8, and 0.6%, respectively.

DISCUSSION

DESCRIPTION OF EQUIPMENT

The equipment consists of an "Electrobalance,"* oxidation and reduction furnaces, a chromatographic column, a thermal conductivity detector, and a recorder. Various electronic components are provided for automatic control and operation. An "Inconel"** 600 combustion tube was used because of its expected long useful life. The equipment is shown in Figure 1.

THEORY OF OPERATION

The operation of the analyzer is based on the Pregl-Dumas technique, modified to provide optimum sample-oxidant contact for combustion under static conditions. A sample of 0.6 to 0.7 mg is weighed into a small aluminum boat on the "Electrobalance" and is covered with a manganese dioxide—tungstic oxide mixture that serves as an oxidant and catalyst. The sample is inserted into the gastight combustion tube where it is oxidized, and the products are analyzed by an automatic sequence of operations.

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* Registered trademark of Cahn Instrument Co.

** Registered trademark of Huntington Alloy Products Division of the International Nickel Co., Inc.

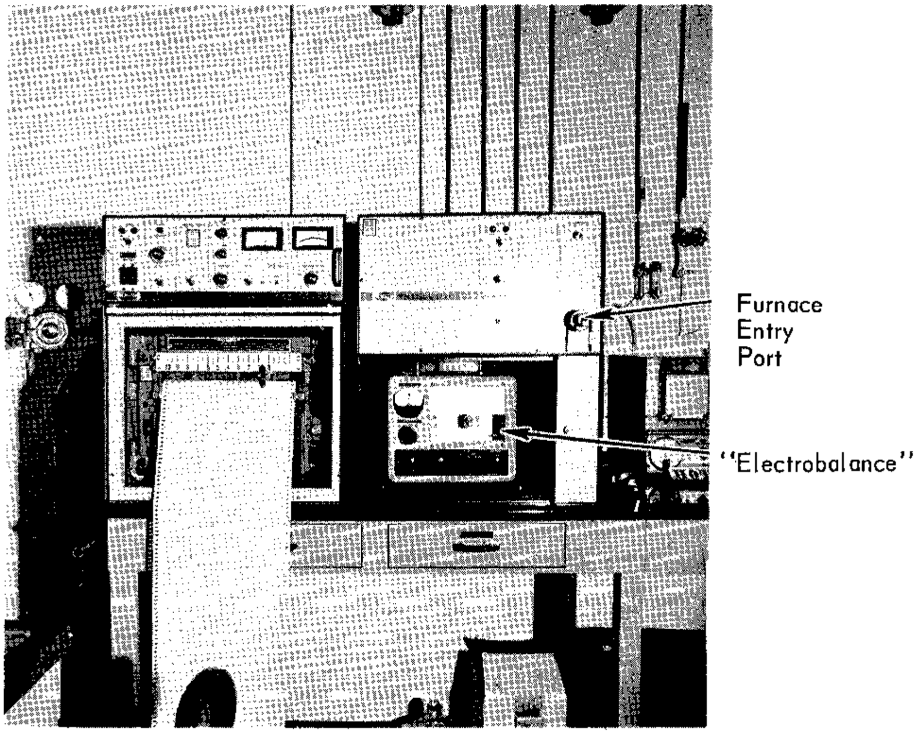


FIG. 1 C-H-N ANALYZER

The sample is oxidized during an initial period of 20 seconds by oxygen from decomposition of the tungstic oxide—manganese dioxide mixture at elevated temperatures.

$$2\ MnO_2 \xrightarrow[1050^\circ C]{WO_3} 2\ MnO + O_2$$

Then, the gaseous oxidation products are swept with helium through columns of hot copper oxide and hot copper metal to oxidize carbon monoxide to carbon dioxide and to reduce nitrogen oxides to nitrogen. Excess oxygen from the combustion step is also removed by the copper metal to prevent subsequent interference.

$$CuO + CO \xrightarrow{1050^\circ C} Cu + CO_2$$

$$Cu + N_xO_y \xrightarrow{450^\circ C} CuO + N_2$$

$$Cu + O_2 \xrightarrow{450^\circ C} 2\ CuO$$

The CO_2, H_2O, and N_2 products are separated on a gas chromatographic column and are determined quantitatively by a thermal conductivity cell. A typical recorder trace of the detector signal for duplicate analyses of a transition metal diphosphonate adduct is shown in Figure 2.

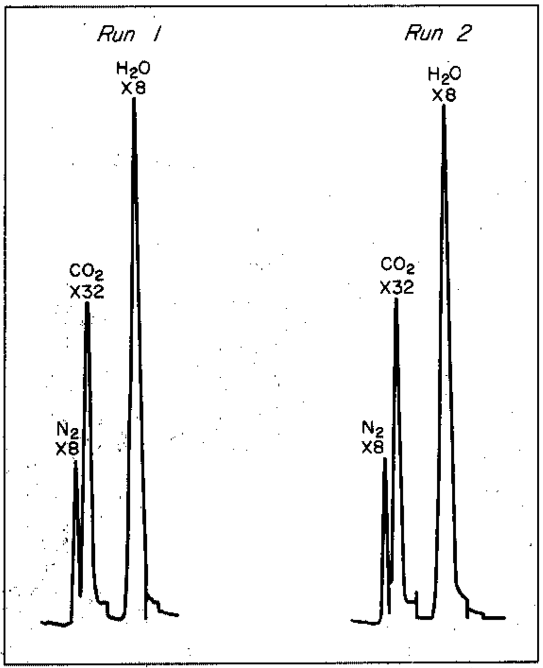


FIG. 2 RECORDER CHART FROM C-H-N ANALYZER

CALIBRATION

Acetanilide, cystine, and melamine obtained from the National Bureau of Standards are used for routine daily calibrations of the analyzer. Calibration factors are obtained by dividing the % C, H, and N in the standard by the peak heights obtained for CO_2, H_2O, and N_2. Sample weights are automatically normalized by a proportioning circuit between the "Electrobalance" and the chromatographic recorder. Peak heights are measured with a scale containing sixty divisions per inch.

The structural formula and elemental composition of the standards are summarized in Table I. Since small variations exist between the calibration factors for the standards, the particular standard used should have approximately the same elemental composition as the samples to be analyzed. Blank values are obtained for the WO_3-MnO_2 catalyst-oxidant, and peak heights are normalized to a common attenuation factor of 32. Data for a typical calibration are summarized in Table II.

TABLE I

Standard Compounds for Calibration

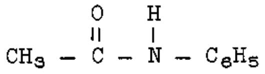
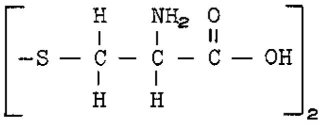
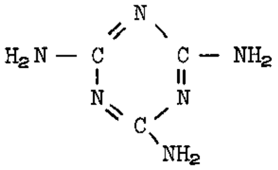
NBS Standard	Structural Formula	% C	% H	% N
Acetanilide	 $CH_3-\overset{\overset{O}{\|}}{C}-\overset{\overset{H}{\mid}}{N}-C_6H_5$	71.09	6.71	10.36
Cystine	 $\left[-S-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{NH_2}{C}}-\overset{O}{\overset{\|}{C}}-OH\right]_2$	29.99	5.03	11.66
Melamine		28.57	4.80	66.64

TABLE II

Typical Calibration Data

	Peak Heights(a)			Calibration Factors(b)		
	Carbon	Hydrogen	Nitrogen	Carbon	Hydrogen	Nitrogen
Blank 1	5.0	14.7	0	-	-	-
Blank 2	5.2	13.7	0	-	-	-
Cystine 1 (0.657 mg)	182	76.2	31.7	0.170	0.0811	0.368
Cystine 2 (0.649 mg)	181	75.7	31.5	0.170	0.0818	0.370
			Avg	0.170	0.0814	0.369

(a) Scale divisions, normalized to attenuation factor of 32.

(b) % C, H, or N, divided by peak height of standard, corrected for peak height of blank.

ANALYTICAL EXPERIENCE

Carbon, hydrogen, and nitrogen determinations were made on many types of organic compounds containing variously oxygen, phosphorus, sulfur, chlorine, fluorine, and transition metals. No serious interferences were found. Several hundred samples, including some liquids encapsulated in aluminum capillary tubing, have now been analyzed successfully. The analysis of several samples by a commercial laboratory using the classical techniques verified the accuracy of the analyzer results, as shown in Table III. The C-H-N analyses obtained for a series of lanthanide complexes of tetraisopropylmethylenediphosphonate are given in Table IV. Theoretical and measured values agree very well.

The highest precision for the C-H-N analyses is obtained with sample weights between 0.6 and 0.7 mg. While values for carbon and nitrogen analyses are constant with sample weights from 0.30 to 0.65 mg, the values for hydrogen are lower by 20% with a 0.3 mg sample. Close control of the flow rate of the helium carrier gas to the gas chromatograph is necessary for good precision. For example, a decrease in flow from 94 to 86 ml/min caused an analytical error of 8%. Under optimum conditions, the precisions for carbon, hydrogen, and nitrogen are, respectively, 0.6, 1.8, and 0.6% (relative standard deviations).

TABLE III

Comparison of C-H-N Analyses(a)

	% Carbon			% Hydrogen			% Nitrogen		
Sample	Theo	SRL	Commercial Lab	Theo	SRL	Commercial Lab	Theo	SRL	Commercial Lab
1(b)	25.60	25.06	25.86	4.27	4.19	4.25	7.46	7.46	6.94
2(b)	31.50	31.08	31.14	5.29	5.19	5.51	12.25	12.34	11.64
3(b)	34.81	33.94	33.85	5.80	5.69	6.18	10.15	9.92	9.53
4(b)	33.10	32.26	32.55	5.52	5.45	5.57	9.65	9.58	10.72
5(c)	30.81	30.74	-	5.97	6.20	-	4.15	4.14	-
6(c)	30.77	31.13	-	5.96	5.91	-	4.14	4.13	-
7(c)	27.00	26.62	-	5.23	5.33	-	4.84	4.50	-

(a) SRL and commercial laboratory values are averages of two results.
(b) Transition metal chelates of diamides.
(c) Rare earth nitrate adducts of diphosphonate esters.

TABLE IV

C-H-N Analyses of Lanthanide Complexes of Tetraisopropylmethylenediphosphonate

Rare Earth	Mole Ratio[a]		Element, %		
			C	H	N
La	2	Theo	30.81	5.97	4.15
		Meas	30.66	6.09	4.14
Ce	2	Theo	30.77	5.96	4.14
		Meas	31.22	5.98	4.13
Pr	2	Theo	30.75	5.96	4.14
		Meas	31.04	5.83	4.05
Nd	2	Theo	30.65	5.94	4.12
		Meas	30.78	5.79	3.99
Sm	2	Theo	30.47	5.90	4.10
		Meas	29.81	5.38	3.94
Gd	2	Theo	30.26	5.86	4.07
		Meas	30.69	5.65	4.05
Tb	2	Theo	30.21	5.85	4.07
		Meas	30.34	5.63	3.94
Dy	1.5	Theo	27.08	5.24	4.86
		Meas	26.79	5.44	4.56
Ho	1.5	Theo	27.00	5.23	4.84
		Meas	26.44	5.24	4.56
Er	1.5	Theo	26.93	5.22	4.83
		Meas	26.10	5.26	4.63
Yb	1.5	Theo	26.75	5.18	4.80
		Meas	25.75	5.29	4.56

(a) Moles organic ligand per mole rare earth

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