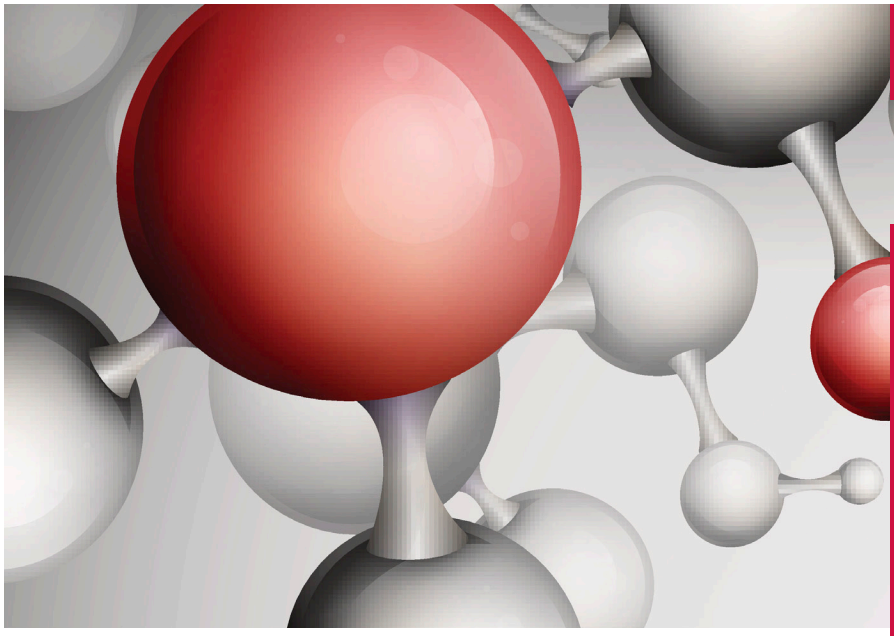

APPLICATION NOTE

Elemental Analysis

Author:

Robert F. Culmo,
Senior Staff Scientist

PerkinElmer, Inc.
Shelton, CT

The Elemental Analysis of Various Classes of Chemical Compounds Using CHN

Introduction

The PerkinElmer PE 2400 CHN Elemental Analyzer[1] is a state-of-the-art elemental analyzer designed for the rapid determination of carbon, hydrogen, and nitrogen content in organic compounds and many other types of materials. The design employs sophisticated solid-state electronics and microprocessor technology, which provide the dual capability to perform the analysis and the computations in a self-contained system. This design is based on our own research and on the cumulative experience of thousands of instrument users over a period of twenty years.

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Improvements made in the analytical design include the three major zones of the system: the combustion area, the gas control area, and the separation and detection area. Enhancements in these areas provide reduced analytical time and improved maintenance and analytical performance of the system. In the combustion area better control and versatility is provided for handling the many classes of chemical materials that exist in industry and research.

The versatile combustion design shown in Figure 1 provides more degrees of freedom for introduction of oxygen. These options include control for oxygen added to the combustion tube before the sample drop, after the sample drop, and during the dynamic phase of combustion. Also, a provision for extending the static combustion time is provided. These time intervals are controlled from 1 second to 300 seconds (5 minutes).

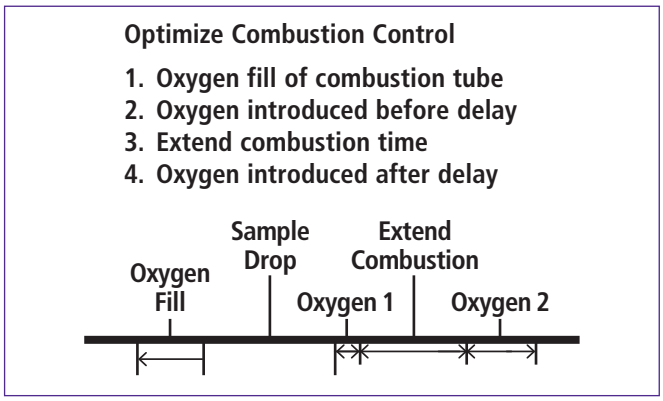

Figure 1. The EA 2400 optimizes combustion by allowing control of several oxygen fill steps

The combination of reagents used in the combustion zone includes chromium oxides, silver tungstate on magnesium oxide, and silver vanadate. These provide both efficient oxidative properties and a high-capacity scrubbing efficiency, ensuring the complete oxidation of volatile products and the effective removal of common interferences.

These features provide the necessary versatility for handling virtually all sample types wherever the determination of carbon, hydrogen, and nitrogen serves a useful analytical purpose. This includes, for example, the analysis of organics, polymers, coals, fuel oils, oil shales, gasoline, ocean sediment, and ocean and air particulates.

This study attempts to answer the question of what happens when various classes of materials are analyzed which are known to be relatively "difficult" to analyze by other instruments or by conventional techniques. This includes materials known to be refractory (difficult to combust) or containing elements or functional groups that interfere with the proper and complete combustion of the compound and with the detection system of the apparatus. These include polynuclear aromatic compounds, steroids, heterocyclic nitrogen derivatives, halogenated and sulfonated compounds, volatile organics, organosilico and phosphorus derivatives, nitro-compounds, organometallics, and pure carbon forms.

Experimental

The results presented were obtained with a standard PE 2400 CHN Elemental Analyzer. The combustion tube packing was supplied with the instrument and consisted of the following components: EA-1000 (chromium oxidizer), silver tungstate on magnesium oxide, and silver vanadate. PerkinElmer Copper Plus (+) and Cuprox were used in the reduction tube. Unless otherwise noted in the discussion, the compounds were sampled in standard fashion using tin capsules for nonvolatile materials and sealed aluminum capsules or pans for liquids and materials having an appreciable vapor pressure. The samples were weighed with a PerkinElmer AD-6 Autobalance.

Results

The following reviews in detail the elemental analysis of various classes of compounds using the PerkinElmer 2400 CHN Elemental Analyzer.

Polynuclear Aromatic Hydrocarbons

Polynuclear aromatic compounds provide a valuable test of an elemental analyzer's capability with respect to accuracy and combustion efficiency because of their exceptional high carbon content. Achieving a result within 0.3% for a 95% carbon content obviously demands more of an analyzer than 0.3% at a more typical 60% level. With other analyzers, linearization of the results is required to achieve the performance found with the PE 2400 CHN (Table I). If the sample size exceeds 2.5 milligrams, the optimize combustion control feature may be used to certify complete sample combustion.

Table 1. Polynuclear Aromatics

Compound	Theory (%)			Found (%)		
	C	H	N	C	H	N
ANTHRACENE	94.34	5.66	--	94.35 94.44	5.64 5.64	--
CHRYSENE	94.70	5.30	--	94.75 94.78	5.25 5.20	--
NAPHTHALENE	93.71	6.29	--	93.72 93.85	6.30 6.35	--

Steroids

Large complex molecules such as steroids produce a variety of combustion fragments when large sample sizes are used. This requires good efficiency from the catalytic combustion reagents. Steroids and related compounds are routinely determined under standard conditions (Table 2).

Table 2. Steroids

Compound	Theory (%)			Found (%)		
	C	H	N	C	H	N
CHOLESTEROL	83.87	11.99	--	83.65 83.68	11. 80 11. 89	-- --
TESTOSTERONE	79.12	9.79		79.25 79.30	9.80 9.79	-- --

Nitro-Compounds

Certain nitro-derivatives have been reported to be a problem because low nitrogen results (0.5 -1.0%) were observed. This problem relates to the observations of Swift[2] who speculated that it was due to the absorption of nitrogen oxides by the copper oxide from the combustion and reduction zones. The translation of his observations to the PE 2400 CHN relates to the produced copper oxide in the reduction zone. This occurs because large amounts of nitrogen oxides are produced with these particular compounds thereby producing the effect observed. Although not proven, it is conceivable that some loss of nitrogen oxides occurs in the reduction zone by absorption or reaction. Specific compounds that have been observed to exhibit this problem include 1-chloro, 2, 4 dinitrobenzene, m-dinitrobenzene, and 2, 4 dinitrophenol. The presence of excess oxygen leads to the generation of nitrogen oxides thereby producing low nitrogen results. To eliminate the possibility of excess oxygen, features of the PE 2400 CHN are used to reduce the amount of oxygen. At the same time the sample size was increased to 4-7 mg. By making these adjustments in conditions, satisfactory results were obtained. This procedure is also useful for determining nitrogen content in explosive materials such as pentaerythritol tetranitrate (PETN).

Table 3. Nitro-Derivatives

Compound	Theory (%)			Found (%)		
	C	H	N	C	H	N
1-CHLORO, 2, 4 DINITROBENZENE	35.54	1.49	13.83	35.60 35.58	1.50 1.48	13.84 13.82
m-DINITROBENZENE	42.86	2.40	16.67	42.79 42.84	2.41 2.42	16.68 16.69

Heterocyclic Nitrogen Derivatives

Heterocyclic nitrogen compounds have historically been classified as being difficult to combust[3] compared to other organics. The nitrogen in the ring requires more vigorous oxidation conditions to ensure complete conversion to the desired products. Results tabulated in Table 4 demonstrate that this problem is not encountered with the PE 2400 CHN.

Table 4. Heterocyclic Nitrogen Derivatives

Compound	Theory (%)			Found (%)		
	C	H	N	C	H	N
CAFFEINE	49.48	5.19	28.85	49.45 49.51	5.18 5.17	28.89 28.95
URIC ACID	35.72	2.40	33.33	35.74 35.72	2.41 2.47	33.34 33.38
UREA	20.00	6.71	46.65	20.14 20.10	6.75 6.68	46.64 46.49
MELAMINE	28.57	4.80	66.64	28.50 28.61	4.81 4.85	66.58 66.59

Polymers

Elemental analysis has been used for a number of years to characterize homopolymers, copolymers, blends, and resin formulations. An elemental analysis for C, H, and N can be the most direct, fastest, and least ambiguous method for determining a copolymer or blend composition. While most of these materials shown in Table 5 present no problems, some polymers can be somewhat refractory. When this is indicated, an additional 2 seconds is recommended for the oxygen fill.

Table 5. Polymers

Compound	Theory (%)			Found (%)		
	C	H	N	C	H	N
NYLON 6	63.68	9.80	12.38	63.58 63.55	9.85 9.91	12.35 12.32
STYRENE/25% ACRYLONITRILE	86.10	7.24	6.60	86.00 6.05	7.28 7.20	6.62 6.65
PTFE	24.00	--	--	23.97 24.10	-- --	-- --

Volatile Organics

Volatile organic liquids can, if they are low boilers, present a problem with encapsulation and combustion. If it is a mixture, such as gasoline, the sample must be sealed instantly.

The sealing unit which provides this capability is the PerkinElmer Liquid Sample Handling Kit (Part Number N241-0149). This unit seals either small capsules (4 µL) or larger capsules (30 µL). When using the small capsules, it is recommended that the sealed vial be placed into a tin capsule prior to entry into the analyzer.

Table 6. Volatile Organics

Compound	Theory (%)			Found (%)		
	C	H	N	C	H	N
n-HEXANE	83.62	16.38	--	83.58 83.59	16.30 16.28	-- --
BENZONITRILE	81.55	4.85	13.59	81.48 81. 46	4.90 4.86	13.61 13.55
GASOLINE*	85.50	14.75		85.45 85.40	14.70 14.80	-- --

** As determined by a commercial testing laboratory.*

Halogenated and Sulfonated Compounds

Elemental analyzers should function with undiminished performance for compounds containing common elements such as halogens and sulfurs. Because of this requirement the PE 2400 CHN Analyzer is designed with a large excess of high efficiency scrubbing reagents -including chromium oxide, silver tungstate, magnesium oxide, and silver vanadate. The ability to obtain results of the quality shown in Table 7 is an impressive feature of the PE 2400 CHN's design.

Table 7. Halogenated and Sulfonated Compounds

Compound	Theory (%)			Found (%)		
	C	H	N	C	H	N
HEXACHLOROBENZENE	25.30	--	--	25.42 25.32	-- --	-- --
PTFE	24.00	--	--	23.97 24.10	-- --	-- --
PHENYLTHIOUREA	55.25	5.25	18.43	55.26 55.28	5.22 5.26	18.44 18.49
p-BROMOACETANILIDE	44.88	3.77	6.54	44.82 44.79	3.78 3.75	6.54 6.57
SULFANILIC ACID	41.61	4.07	8.09	41.59 41.60	4.08 4.06	8.10 8.11
CYSTINE	29.99	5.03	11.66	30.10 30.01	5.06 5.09	11.67 11.65

Organosilico and Organophosphorus Compounds

The presence of hetero elements such as silicon or phosphorus can lead to the formation of refractory complexes with carbon. Of these, silicon is potentially the most troublesome. It can form the extremely stable silicon carbide or a volatile stable silane. Pregl[4] and Belcher[5] have reported that these problems could be overcome by mixing either vanadium pentoxide or tungsten oxide with the weighed sample. Generally, however, using tin capsules (which generate a vigorous exothermic reaction) is sufficient for handling these derivatives with the PE 2400 CHN, as indicated in Table 8. If additional vigor is required, 5-10 mg of vanadium pentoxide can be added to the weighed sample.

Table 8. Organosilico and Organophosphorus Compounds

Compound	Theory (%)			Found (%)		
	C	H	N	C	H	N
TRIPHENYL PHOSPHINE	82.43	5.76	--	82.35	5.77	--
				82.31	5.79	--
TETRAMETHYL-DISILOXANE	35.76	10.50	--	35.77	10.51	--
				35.78	10.57	--

Organometallic Compounds

By conventional CHN techniques, organometallic compounds often exhibit low carbon values because of the possible formation of stable metal carbonates and metal carbides. In addition, metal residues can cause a deterioration and possible poisoning of conventional combustion tube ingredients. These problems were resolved previously with the PerkinElmer 240 Series Elemental Analyzer by the addition of chemical aids to the weighed sample and by the combustion packing design[6]. These conditions and reagents have been incorporated in the PE 2400 CHN design so that such materials are again analyzed routinely with the use of tin capsules. However, if additional vigor is required for oxidizing the sample, 5-10 mg of an oxidizer can be added to the weighed sample.

Table 9. Organometallic Compounds

Compound	Theory (%)			Found (%)		
	C	H	N	C	H	N
POTASSIUM ACID PHTHALATE	47.05	2.47	--	47.10	2.45	--
				47.08	2.46	--
BIS (ETHOXY-DIPHENYL-PHOSPHINE) DECARBORANE	57.90	7.29	--	57.85	7.30	--
				57.92	7.28	--

Miscellaneous Sample Types

The PE 2400 CHN's flexible optimize combustion feature is utilized for large sample sizes and refractory materials. This feature is ideal for pure carbon forms. A combination of additional oxygen and extended combustion times is required for these materials. For example, the carbon sample runs shown in Table 10 were 1.7 and 2.2 mg (sample size) and required:

1. Oxygen Fill 5 seconds
2. Extend Combustion 20 seconds
3. Oxygen Boost 1 2 seconds
4. Oxygen Boost 2 0 seconds

Additionally, it is recommended to raise the combustion furnace to 975 °C.

Table 10. Miscellaneous Sample Types

Compound	Theory (%)			Found (%)		
	C	H	N	C	H	N
CARBON FIBER	100.00	--	--	99.85	--	--
				99.89		

Discussion

The PE 2400 CHN is specified to achieve results within 0.3% on pure standard organic materials where sample size is in the range of 1 to 3 milligrams.

Q **How often must the system (instrument, balance, gases, reagents) be calibrated with a known standard to achieve this accuracy?**

A We recommend a check twice a day, but experience has shown that an instrument used continuously seldom requires this frequency. It is still good practice to check calibration at least once a day even though the calibration factors have been essentially constant for many days if only for advance indication of the need to replace tube packings.

Q **Can accuracy be improved by increasing sample size to produce larger signals at the detector?**

A The answer is yes, but within limits. Sample size cannot be increased indefinitely as the supply of oxygen for combustion is limited. For easily combustible samples with low carbon content (30-40%), one can use up to 10 milligrams of sample material. For unknowns, however, it is still prudent to use less than 3 milligrams. When the results or the combustion efficiency are in question, it is good practice to run a duplicate at a significantly different weight level (1 and 3 milligrams, for example). If a combustion problem is evident, optimization of the combustion conditions may be required. Because the PE 2400 CHN provides more degrees of freedom for combustion control, virtually all sample types are more easily handled. For example, as shown in Figure 1, the operator may add more oxygen to the combustion time, and add more oxygen during the dynamic phase of combustion.

Q **What about analysis for low levels of C, H, or N in a non-combustible matrix -an oil shale, for example?**

A This is quite a different matter than the case for pure combustible samples and neither the 0.3% absolute accuracy specifications nor the sample size limitations apply. The accuracy achievable in such a case depends upon how much sample can be introduced into the instrument and still combust all of the combustible content. For example, a pulverized rock, shale, or soil sample containing 5% can be used in amounts up to 100 milligrams or more to produce signal levels comparable to those of a few milligrams of pure organic material. In this case, the accuracy of determination as a percent of the total sample would be at the +/-0.01% level. Specific examples of such cases will be given in subsequent studies.

This study attempts to answer the question of what happens when various classes of materials are analyzed which are known to be relatively "difficult" to analyze by other instruments or by conventional techniques. This includes materials known to be refractory (difficult to combust) or containing elements or functional groups that interfere with the proper and complete combustion of the compound and with the detection system of the apparatus. These include polynuclear aromatic compounds, steroids, heterocyclic nitrogen derivatives, halogenated and sulfonated compounds, volatile organics, organosilico and phosphorus derivatives, nitro-compounds, organometallics, and pure carbon forms.

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PerkinElmer, Inc.
940 Winter Street
Waltham, MA 02451 USA
P: (800) 762-4000 or
(+1) 203-925-4602
www.perkinelmer.com

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