

focus on Laboratory Products

Implications of Instrument Design on CHN Microanalysis Data Quality

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The analysis of milligram quantities of organic compounds to precisely and accurately quantify percentage carbon (C), hydrogen (H) and nitrogen (N) content has a history dating back over 90 years [1, 2].

CHN microanalysis is today widely acknowledged as a quick and inexpensive analytical technique for determining the purity of a compound. The technique is widely applicable, ranging from the pharmaceutical industry through synthetic chemistry to environmental monitoring. CHN microanalysis can be also used to fully characterise compounds when used in conjunction with techniques such as NMR and Mass Spectrometry.

All CHN microanalytical applications need repeatable high data quality as well as instrument reliability, productivity and ease of use. Unfortunately only certain CHN microanalysis instrument designs appear able to deliver these goals.

Background to the Technique

The sample methodology and chemistry which CHN microanalysis is based upon is common to most systems. Typically a sample weight of 0.3 - 3 milligrams is weighed into a tin capsule which is introduced into a high temperature furnace. The sample is combusted in oxygen resulting in an exothermic reaction elevating the combustion temperature to 1800°C [3].

The resultant sample combustion products pass through oxidation reagents [4] to produce carbon dioxide (CO₂), water (H₂O), nitrogen (N₂) and nitrogen oxides (N_xO). These gaseous products are then passed over heated copper to remove excess oxygen and to convert the nitrogen oxides back to nitrogen. The oxidation reagents used by various commercial CHN microanalysis systems differ, but all serve the same primary purpose i.e. sample oxidation.

The carrier gas used in CHN microanalysis is helium, although some systems can use Argon as an alternative but this normally leads to significant losses in sensitivity.

It is in the orientation of sample introduction into CHN microanalysers and in the detection / measurement of the combustion products where the systems vary most markedly. Today, commercially available CHN microanalysis systems fall broadly into 3 categories - static, dynamic and hybrid.

Static system

The general methodology / chemistry is as previously described [3].

In a static system (see *Figure 1a* below) the mixture of combustion products (CO₂, H₂O and N₂) are pulsed into a mixing volume with the carrier gas (He) to ensure a homogeneous mixture at constant temperature and pressure. The pulsing of the combustion products into the mixing volume speeds up the formation of a homogenous mixture which contributes to faster analysis times. The pressure of the mixture is monitored by a transducer and at a set pressure, the homogeneous mixture is released into a known sample volume. This known volume of combustion products then passes through a series of traps where CO₂ and H₂O are completely absorbed with high precision thermal conductivity detectors located before and after each absorption trap. The difference between the output of each set of detectors is directly proportional to the quantity of each trapped component (CO₂ and H₂O) thereby enabling the quantity of carbon and hydrogen in the original sample to be determined. The remaining component of the combustion products (nitrogen) is measured with reference to pure helium carrier gas. The difference in thermal conductivity is thus proportional to the nitrogen content. Detection is in the steady state and thus highly accurate and precise. Quantification of CO₂, H₂O and N₂ is achieved via integration of a steady detector signal over several seconds. Static systems have been proven to be highly reliable in 1000's of installations worldwide.

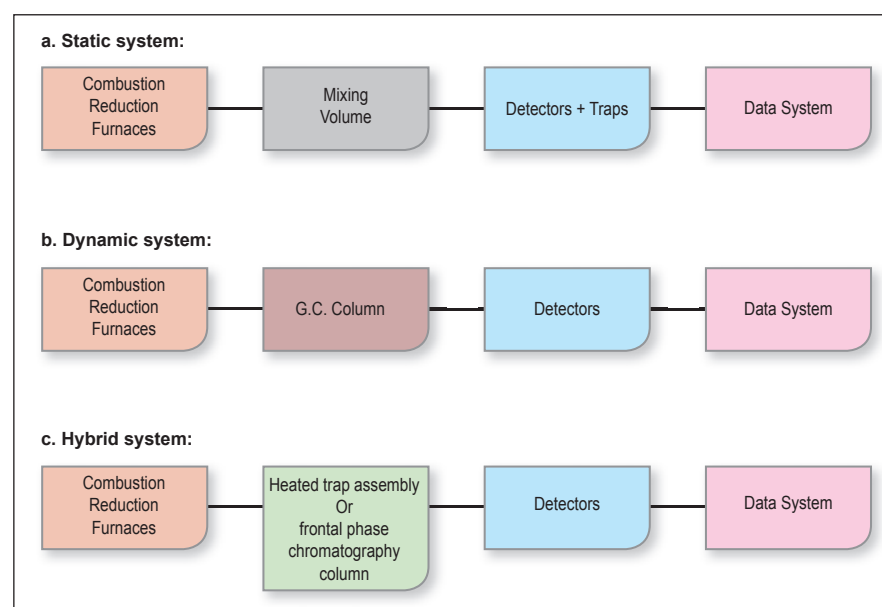


Figure 1. CHN Microanalysis system (layout schematics)

Dynamic system

The general methodology / chemistry is as previously described [3].

The analysis process proceeds as follows in a dynamic system (see *Figure 1b* above). After going through the normal oxidation / reduction process the mixture of combustion products [4] (CO₂, H₂O and N₂) are then passed through a gas chromatographic column to separate the components. This results in a gas chromatogram of three peaks eluting in the order of N₂, CO₂, and H₂O (see *Figure 1b*). In dynamic systems, measurement of the integrated area under each eluting gas chromatogram peak from the sample being determined is referenced against compounds of known CHN content. Loss of precision can sometimes occur in dynamic systems due to degradation of the chromatographic columns over time and when analysing samples with high hydrogen content due to tailing of the H₂O peak making area integration less accurate. Also analysing larger sample weights greater than 10 milligrams (dependent on CHN content) with a dynamic system can result in poor chromatographic separation (unresolved peaks). By comparison, in a static system the CO₂, H₂O and N₂ are determined by a simple linear voltage measurement of a steady signal that provides constant high precision thereby eliminating the shortfalls of the dynamic system.

Hybrid systems

The general methodology / chemistry (oxidation/reduction process) is as previously described.

Currently two commercial CHN microanalysis systems are available that use hybrid designs. Both are vertical furnace designs where the sample is dropped into the furnace via gravity.

The first hybrid microanalysis system design (see *Figure 1c* above) employs gas chromatographic separation where the peaks are purposely not fully resolved and measurements are taken between the partially resolved peaks. This is known as frontal phase chromatography. Thermal conductivity measurements are taken to quantify each component. Microanalysis systems based on frontal phase chromatography, offer the benefit of increased speed of analysis. However by running the CHN microanalysis faster you potentially compromise data quality, particularly the fits eluting nitrogen determination, because the eluting peaks are only partial resolved.

The second hybrid microanalysis system design uses a heated trap to capture the combustion products which are then released by thermal desorption. In this microanalysis system design, nitrogen passes straight through the trap and all other components are trapped and then thermally desorbed over time. Thermal conductivity measurements are used to quantify each component (C, H and N). Hybrid systems incorporating heated trap technology offer the potential of measuring carbon, hydrogen, nitrogen and sulphur simultaneously. However this is often at the expense of data accuracy and precision particularly at sub-milligram sample weights.

Different Instrument Designs - Advantages and Disadvantages

The need for the best achievable data accuracy, precision and long-term stability when determining CHN content has become vitally important in order to comply with more stringent quality practices and for routine determination of sub-microgram samples in some industry sectors. As previously discussed, there are a number of different CHN microanalysis system designs [3] (dynamic, hybrid and static measurement systems) all of which can be demonstrated to produce accurate and precise data. However the consequences of the aforementioned differences in instrumental design becomes significant when they are challenged with producing long term reliable data from unknown samples in a real laboratory environment. Most CHN microanalysis systems can produce excellent accuracy when the result is based upon the mean of several analyses. However it is a very different challenge when analysing unknown samples in a busy laboratory tasked with running hundreds of samples per month where the need to always run replicate samples is not a realistic methodology.

Combustion orientation

A notable design difference in commercially available CHN microanalysis systems is that of the orientation of the combustion furnace.

While the Exeter Analytical 440 employs a horizontal combustion furnace, all other dynamic and hybrid systems operate with a vertical arrangement. With the horizontal furnace arrangement, samples are introduced into the combustion tube on a quartz ladle which critically enables the removal of all sample residue after combustion. In a vertical furnace arrangement the samples are dropped into the combustion tube and combusted on top of previously combusted samples.

When a laboratory undertakes to carry out a CHN analysis, the purpose of the analysis is to acquire a set of analytical data representative of that sample. There is no analytical justification to combust a sample on top of previously combusted samples as it can lead to inferior analytical data. The build-up of sample residue in the combustion zone of vertical furnace systems considerably increases the potential for poor analytical data. Long-term stability is compromised and spurious results are likely to be generated due to memory effects from certain sample types. As sample residues collect in the combustion tube (see *Figure 2* below) the flow characteristics of the combustion tube change. Changing flow characteristics has a particular impact on dynamic CHN microanalysis systems as they depend on constant gas flow. Any change in gas flow has a direct effect on calibration characteristics and stability.

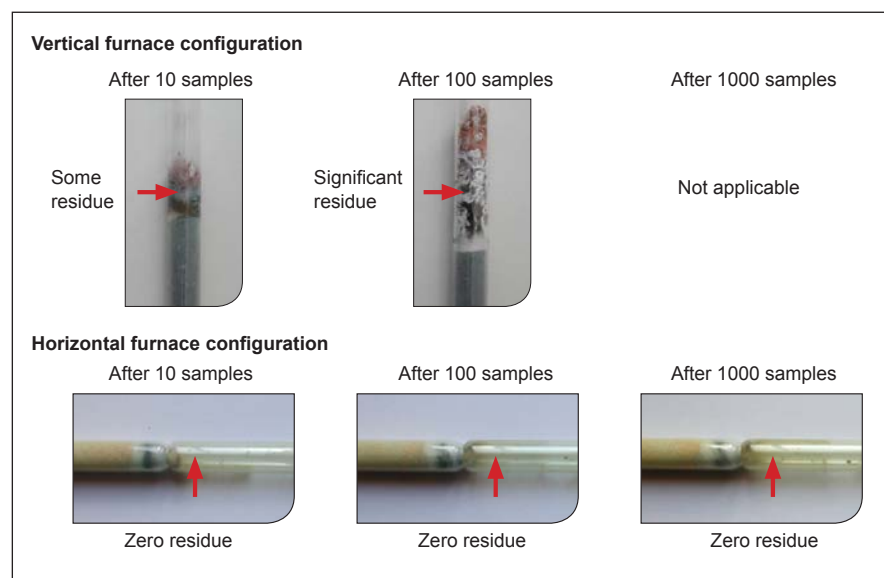


Figure 2. Effect of combustion tube orientation on residue build-up

Build-up of sample residue in a CHN microanalysis system is an important consideration where a sample combusts slowly or where a large volume of residue is produced by each sample such as is found in filter or waste materials analyses [5, 6].

Carbon fibres, which are found in many modern day composite materials, are an example of a sample that requires time to fully combust. The combustion of carbon fibres is not only a function of temperature but also of time. Most vertical furnace analysers typically do not combust refractory type materials such as carbon fibres very well, because insufficient time exists in their combustion process for complete combustion. This is easily demonstrated if a blank is run directly after a refractory sample such as carbon fibres. In such instances blank values are elevated due to the sample that was left in the residue from the previous combustion now burning along with the next sample, in this case a blank. The consequent effect on sample data is falsely elevated carbon values.

In a horizontal furnace design memory effects from samples such as carbon fibres do not occur. Firstly, the residue is removed between each sample analysis preventing memory effects. Secondly in horizontal systems, such as the Model 440 from Exeter Analytical, complete control over the combustion process enables the analyst to extend combustion time and oxygen flow to ensure total sample combustion.

Factors Affecting Data Quality

A series of experiments were carried out to demonstrate the performance of a horizontal furnace CHN microanalysis system, in this case an Exeter Analytical Model 440. The key areas that are known to affect data quality are:

- Accuracy and precision
- System stability
- Diverse sample types
- System linearity
- Demanding sample types
- CHN versus CHNS measurements
- Ease-of-use

Accuracy and precision

The most important CHN microanalysis criteria for many analytical laboratories is to ensure optimal accuracy and precision across a wide range of sample types. A user does not want to set up their analyser with different operational parameters for every different sample type they may come across. In today's busy scientific world there is constant pressure to maximise laboratory productivity.

In the UK, the independent Royal Society of Chemistry, Microanalytical Group [7] runs programs to test achievable data accuracy and precision on current commercially available CHN microanalysis systems located in real working laboratories. In *Figure 3* below we show a set of data, run on an Exeter Analytical Model 440, used by the Microanalytical group as the benchmark for accuracy and precision testing.

Sample Run	%C	%H	%N
1	65.43	6.72	8.45
2	65.47	6.73	8.45
3	65.47	6.72	8.48
4	65.45	6.70	8.44
5	65.44	6.72	8.47
6	65.50	6.72	8.52
7	65.52	6.70	8.52
8	65.48	6.70	8.49
9	65.45	6.70	8.48
10	65.49	6.71	8.48
Mean Values	65.47	6.71	8.48
Theoretical Values	65.44	6.71	8.45
Deviation from theory	0.03	0.00	0.03

Operating details: Combustion temperature 975°C; Reduction Temperature 600°C; Oven temperature 81°C; Combustion time 60 seconds; Weighing capsules high purity tin; calibration standard OAS Acetanilide

Figure 3. Accuracy and precision (horizontal furnace design)

The test data in *Figure 3* can be clearly seen to satisfy one standard deviation from the theoretical values of the test compound accepted as true values. The routine achievability of producing such data quality highlights the excellent accuracy and precision available from a horizontal furnace design.

A horizontal furnace design CHN microanalysis system has achieved the best accuracy and precision in each of the last three independent Royal Society of Chemistry, Microanalytical group tests [7].

System Stability

Nearly all commercially available CHN microanalysis systems can be demonstrated to give acceptable data accuracy and precision on selected samples. However, a truer reflection of the real data quality a user can expect to achieve in working laboratory conditions may be demonstrated by a longer-term stability test. Instability in a CHN microanalysis system over time will result in data straying outside acceptable limits of accuracy and precision. This will result not only a reduction in data quality, but also a marked increase in the time spent on sample re-runs and equipment recalibration.

The longer-term stability of the Exeter Analytical Model 440 was tested in actual laboratory conditions. A run of 60 samples was placed in the system and the calibration constants calculated. The calibration constant relates the number of microvolts detected to each microgram of element. The run of 60 samples (including 11 standards) was analysed under normal conditions. To maintain an accuracy of 0.3% absolute the maximum deviations of the calibration constants allowed should be approximately C=0.08, H=2.75, N=0.22. The data in Figure 4 below, run on the Exeter Analytical Model 440 shows that all calibration constants easily met the criteria for good longer-term instrument stability.

Carbon Calibration Factor	Hydrogen calibration factor	Nitrogen calibration factor
21.18	66.68	7.52
21.16	66.73	7.53
21.17	66.74	7.51
21.19	66.50	7.51
21.18	66.20	7.50
21.17	66.14	7.50
21.18	66.14	7.49
21.16	65.92	7.48
21.18	66.42	7.50
21.18	66.30	7.51
21.18	66.77	7.52

Operating details: Combustion temperature 975°C; Reduction Temperature 600°C; Oven temperature 81°C; Combustion time 60 seconds; Weighing capsules high purity tin; calibration standard OAS Acetanilide

Figure 4. Horizontal Furnace – test of longer term instrument stability

Diverse sample types

To demonstrate how a horizontal furnace system copes well with a wide range of samples without need for constant recalibration, the Exeter Model 440 CHN Microanalysis system was set up to sequentially run a series of 8 diverse samples (see Figure 5 below).

Compound	Theory (%CHN)	Results	Comments
Stearic Acid 99%	75.99, 12.76, 0.00	76.15, 12.60, 0.03 76.09, 12.61, 0.01	High percentage Hydrogen content
L-Tryptophan OAS	64.69, 5.92, 13.72	64.64, 5.98, 13.71	Amino Acid
S-Benzyl Thiuronium Chloride, OAS	47.40, 5.47, 13.82	47.48, 5.48, 13.80 47.40, 5.50, 13.79	Contains Chlorine and Sulfur
Disodium Ethylene-Diamine Tetraacetate, ACS	32.27, 4.84, 7.53	32.15, 4.85, 7.49	Chelating agent
Melamine, Lab grade.	28.57, 4.80, 66.64	28.77, 4.84, 66.55 28.75, 4.86, 66.52	Heterocyclic Nitrogen derivative
4-Fluorobenzoic Acid OAS	60.01, 3.59	59.94, 3.82 59.95, 3.82	Contains Fluorine
Chlorodinitrobenzene OAS	35.58, 1.49, 13.83	35.55, 1.59, 13.63 35.56, 1.57, 13.70	Poly Nitro Compound
N-(2-Chloro-4-Nitrophenyl) N'-(4-Iodophenyl) Thiourea 99%	36.13, 2.10, 9.65	36.08, 2.22, 9.70 36.09, 2.24, 9.68	Complex compound containing Iodine, Chlorine, Sulfur

Operating details: Combustion temperature 975°C; Reduction Temperature 600°C; Oven temperature 81°C; Combustion time 60 seconds; Weighing capsules high purity tin; calibration standard OAS Acetanilide.

Figure 5. Sequential analysis of diverse sample types

The results demonstrate how by eliminating sample-to-sample carry over effects the Exeter Model 440 CHN microanalysis system is able to produce excellent data from a diverse and challenging set of diverse samples run sequentially without need for constant system adjustments.

System linearity

Ensuring CHN microanalysis system linearity is crucial in generating top quality data as the elemental content of unknown samples can be considerably different to that of your analytical standards.

The Exeter Model 440 CHN microanalysis system however beneficially uses single weight calibration as its detector response is very linear.

The graphs in Figure 6 below demonstrate the excellent Carbon, Hydrogen and Nitrogen linearity (linear coefficients are 0.9999 or better) routinely achievable on the Model 440 CHN microanalysis system.

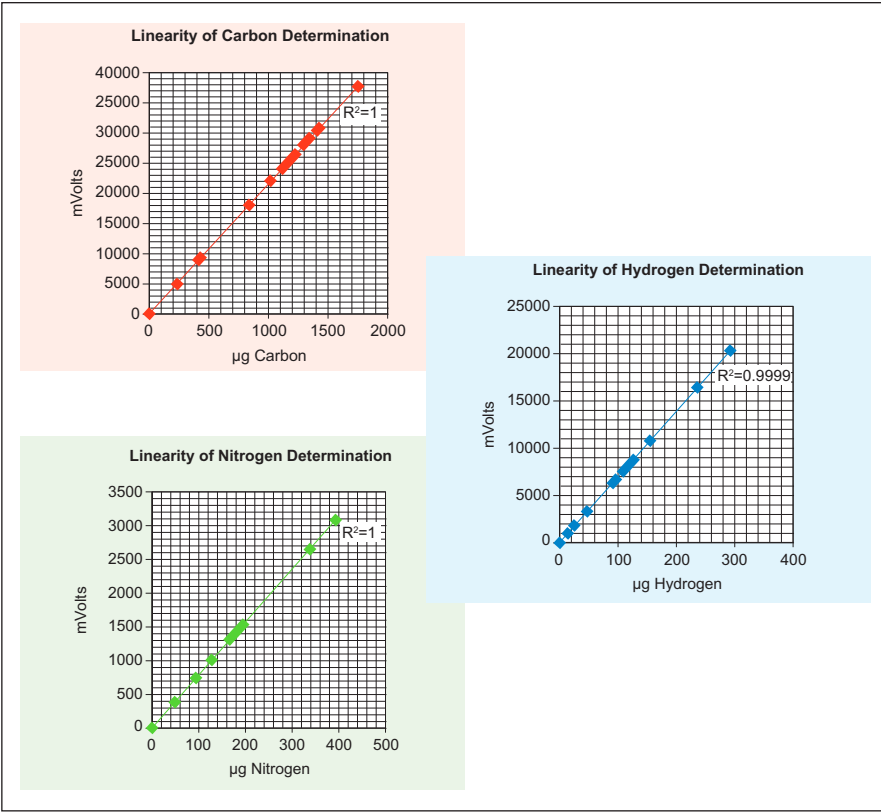


Figure 6. Carbon, Hydrogen & Nitrogen Linearity

Demanding sample types

Considerable variance in CHN microanalysis system performance can also be seen with more demanding samples. The example of time dependent combustible samples, earlier in this article, gave an example of how horizontal furnace systems provide considerably better results with certain samples [6, 8, 9].

In this section we consider other demanding sample types (volatile liquids, highly fluorinated compounds, filter samples and air sensitive samples) that demonstrate a clear difference in the data that is achievable by horizontal as compared to that from vertical furnace CHN microanalysis systems.

Volatile liquids

Horizontal furnace CHN microanalysis systems are widely used in petrochemical and contract analysis laboratories as they offer the ability to use rigid wall tin containers for the routine analysis of volatile liquids.

Horizontal furnace CHN microanalysis systems allow sample residue to be removed between each sample, thereby eliminating the chance of residue build up from the heavier rigid wall containers that are necessary for volatile liquid analysis. The use of rigid wall tin containers allows samples to be sealed with a cold weld device that enables routine encapsulation of highly volatile, hygroscopic and even air sensitive samples. The results in Figure 7 below were derived from analysis of a volatile fuel sample, sealed for analysis using a cold weld sealing device. Ten samples of the volatile fuel were analysed to demonstrate achievable data accuracy and precision.

Sample Run	%C	%H
1	86.90	13.07
2	87.05	13.14
3	86.94	13.15
4	86.94	13.14
5	87.00	13.12
6	86.90	13.12
7	86.68	13.06
8	86.84	13.07
9	86.75	13.03
10	87.01	13.13
Mean Values	86.90	13.10

Operating details: Combustion temperature 975°C; Reduction Temperature 600°C; Oven temperature 81°C; Combustion time 60 seconds; Weighing capsules high purity tin; calibration standard OAS Acetanilide.

Figure 7. Attainable accuracy and precision on volatile samples

Highly Fluorinated Samples

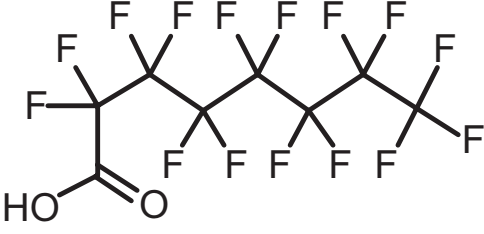
Generally compounds containing fluorine can be successfully analysed for percentage CHN content on most CHN microanalysis systems under standard operating conditions. The magnesium oxide in the combustion tube reagent packing absorbs fluorine as HF, and releases the Hydrogen. However, highly fluorinated compounds are often difficult to combust and consequently can yield incorrect carbon and high nitrogen data.

There are two current theories as to why this happens:

- 1) Due to the strength of the C-F bond. CF_2 passes through the combustion tube packing if not fully oxidised. The CF_2 is then detected as nitrogen, resulting in both low carbon and high nitrogen.
- 2) Fluorine reacts with silica from the combustion tube and forms SiF_4 which is volatile and is detected along with nitrogen, thereby causing similar problems to the first theory.

Gas chromatography based CHN microanalysis systems have particular difficulties in accurately analysing highly fluorinated materials as measurement of the nitrogen peak can be affected by the by-products of the combustion process causing interferences.

Reliable data from highly fluorinated compounds can however be generated using sample additives, such as magnesium oxide or red lead (Pb_3O_4), and running the analysis on a horizontal furnace CHN microanalysis system (see *Figure 8* below).



	%C	%H	%N
Theory	22.05	0.24	0.00
Found	22.10	0.26	0.00

Figure 8. CHN determination on Perfluoro-N-Octanoic acid (95%)

Filter Sample Analysis

A horizontal furnace CHN microanalysis system, such as the Exeter Analytical Model 440, has significant advantages when analysing filter samples. These advantages are primarily due to its horizontal furnace design which eliminates sample residue build up in the combustion tube after each sample is combusted. This results in enhanced data accuracy and sample throughput, as there is no need to replace the combustion tube frequently as is required in vertical systems.

Standard practice on filter samples analysed on vertical microanalysis systems is for the filters to be sub-sampled several times. This results in rapid residue build up and can require cleaning the combustion tube after as little as 20 samples. By contrast, filters of up to 50mm in diameter can be analysed with no need for sub-sampling on the Exeter Analytical Model 440 – a horizontal furnace design system. The Model 440 routinely is able to run in excess of 1000 samples through its combustion tube before changing the tube is required.

This makes running filter samples considerably easier on the Model 440 when compared with vertical furnace systems where filters must be sub-sampled [5, 10, 11, 12].

Air Sensitive Samples

The ability of a horizontal furnace CHN microanalysis system, such as the Exeter Analytical Model 440, to run samples sealed in rigid wall capsules makes the running of air sensitive samples routine.

Locating your cold weld capsule sample sealer in a glove box under an inert atmosphere is the key to good sample preparation of air sensitive materials. Once air sensitive samples are sealed using the cold weld sample sealer they can be handled by the Model 440 like any normal sample. The sample is completely sealed inside the tin capsule. A representative blank should be run.

	time=0	time=20 mins
%C	15.31	15.20
%H	14.20	14.32
%N	33.51	33.37

Figure 9. CHN determination of air sensitive organometallic compound

This data demonstrates the effectiveness of the cold weld device in combination with rigid wall capsules to securely encapsulate air sensitive samples and the Exeter Analytical Model 440's ability to generate repeatable high accuracy CHN data from such samples.

Thermally Stable Materials

Because of the high temperatures required to combust thermally stable materials such as many carbides and nitrides, it can be difficult to obtain accurate and precise CHN analytical data on some systems.

To obtain precise, accurate CHN data from thermally stable materials, the complete control of the combustion process (amount of Oxygen used and time taken) is of paramount importance. Also the ability to use combustion enhancing additives, such as high temperature flux (a mixture of NaF and Pb_3O_4) can be helpful.

Due to the dynamic design of most vertical furnace designs you have a lack of control over the combustion parameters. This is particularly true for the amount of oxygen delivered for sample combustion as well as the time allowed for complete combustion. A vertical furnace design severely limits the user as to the additives one can add to aid the combustion process for thermally stable materials. This is due to residue build up which can result in both unstable calibration and low sample recovery.

By contrast the operating software on the Exeter Analytical Model 440 CHN microanalysis system allows complete control over oxygen addition and combustion time. As previously discussed the addition of additives, in this case a high temperature flux that elevates the temperature of combustion to approximately 2300°C, is not a problem on a horizontal furnace design system.

Typical analytical data for a refractory material (silicon carbide) is shown in *Figure 10* below with and without combustion parameter control and addition of flux additive.

	%C
Theory	29.43
No Flux additive	20.11 21.05
Flux additive used	29.37 29.60

Figure 10. High Temperature C determination on Silicon Carbide

CHN Versus CHNS

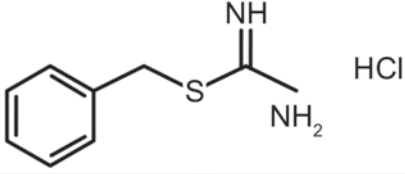
The ability to accurately determine percentage sulphur levels in addition to percentage carbon, hydrogen and nitrogen is desirable, especially in the petrochemical and pharmaceutical industry where compounds containing sulphur are common.

Unfortunately no commercial microanalysis system can routinely produce accurate and precise C, H, N and S data across a wide range of samples. The reality of this conundrum is that achievable sulphur data is not as good as the CHN data that these systems can produce.

There are fundamental chemistry issues with the variable ratio of sulphur dioxide and sulphur trioxide formed by combustion. This is matrix dependent and leads to difficulties with accurate calibration over a range of different sample types. Higher temperatures are required to convert the sulphur to sulphur dioxide efficiently than is currently possible on present day microanalysis systems.

If your requirement is for repeat batch analysis of the same material, then accurate sulphur determination is possible as you will be able to set up accurate calibration as any losses due to sulphur trioxide should be consistent.

However for labs looking to achieve high CHNS data quality across a range of samples then using a CHN microanalysis system in combination with oxygen flask combustion followed by titration or ion chromatography offers excellent results (see *Figure 11* below) [13, 14].



	%C *	%H *	%N *	%S **
Theory	47.40	5.47	13.82	15.82
Found	47.40 47.42	5.47 5.45	13.78 13.81	15.82 15.89

* %CHN found by Model 440 Elemental Analyser
** %S found by Oxygen Flask combustion

Figure 11. CHNS determination on S-Benzylthiuronium Chloride

Ease of Use

Ease of use is a commonly made claim from almost all microanalysis instrument suppliers. This claim has many contributory factors including simple measurement of accurate and precise results, ability to cope with wide ranging sample types and design features eliminating the need for constant system re-optimisation.

The Exeter Analytical Model Model 440 Elemental Analyser with its horizontal furnace design is a fully automated CHN/O/S elemental analyser. The system and its Windows based operating software has been designed to reduce human error and incorporates extensive automation and diagnostic processes, along with comprehensive reporting facilities, enabling easy integration into other software packages. In today's laboratory environment such features should be considered as a minimum requirement of any analytical system.

Conclusion

Elemental microanalysis that can produce accurate C,H,N composition data on unknown samples continues to be a broadly applicable and valuable analytical technique. In this article I have looked to demonstrate that results from CHN microanalysis systems of different design can vary considerably.

The Exeter Analytical Model 440 has been shown to be routinely able to simply produce accurate and precise data on wide ranging sample types, over long periods of time without system re-optimisation. The application examples above also show how a horizontal furnace microanalysis system design give accurate and precise CHN data, without the inherent problems associated with vertical furnace design systems.

The Author

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