C,H,N MICRO-ANALYSIS: A COMPARATIVE REVIEW OF THE EFFECTS OF INSTRUMENT DESIGN ON ANALYTICAL PERFORMANCE

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Key Words: CHN Analysis, Micro-Analysis, Combustion, Reduction, Accuracy, Precision, Stability, Ease of Use.

Introduction

The origin of accurate elemental analysis of milligram quantities of organic compounds can be traced back to the 1923 Nobel Prize winning work by Pregl[1,2].

During the ensuing forty years the development of new global synthetic chemical industries created an escalating demand for elemental microanalysis. As demand to analyse greater numbers of samples rose the need to automate the micro-analytical procedures whilst maintaining the accuracy and precision of the classical techniques became apparent. The 1960's [3] saw the introduction of the first automated elemental analysers, which quickly gained acceptance in laboratories throughout the world. Today the requirements for high data quality, reliability, system productivity and ease of use has placed demands on analysts and instrument designers alike. Only certain micro-analytical instrument designs appear able to deliver these goals

Sample preparation & combustion chemistry

The sample preparation methodology and combustion chemistries [3,4] used by different instrument designs are generally similar. To analyse a sample a weighed (1-2 mg) quantity is introduced into a high temperature furnace and the sample is combusted in oxygen. Typically the sample is weighed into a tin container, which gives the advantage of strong exothermic combustion ensuring complete sample oxidation at approximately 1800 ° C. The resulting combustion products pass through specialised oxidation reagents, to produce from the elemental carbon, hydrogen, and nitrogen, carbon dioxide (CO_2), water (H_2O), nitrogen (N_2) and N oxides respectively. These gases are then passed over copper to remove excess oxygen and reduce the oxides of nitrogen to elemental nitrogen[2]. Helium is used as the carrier gas. Other elements present are removed by the use of specialised combustion reagents [4].

Detection of Combustion Products

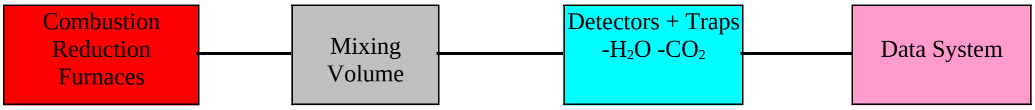
It is in the detection and measurement of a samples combustion products that micro-analytical systems differ most markedly. CHN micro-analytical systems broadly fall into two categories - static and dynamic.

Static system

In a static system (Figure 1) the sample is introduced via a ladle into the combustion tube into a pure oxygen environment, after combustion has occurred the sample residue is removed from the combustion tube. The mixture of combustion products (CO_2, H_2O and N_2) is pulsed into a mixing chamber to ensure a homogeneous mixture at constant temperature and pressure. The procedure of pulsing the combustion products into the mixing chamber speeds up the formation of a homogenous mixture which contributes to faster analysis times. The pressure of the mixture is typically monitored by a pressure transducer and a known volume of the product mixture released when a pre-set pressure is reached (e.g. 1500mm Hg). This known volume of combustion mixture then passes through a series of traps where H_2O and CO_2 are completely absorbed, with high precision thermal conductivity detector filaments located before and after each absorption trap (Figure 2). The difference between the output of each set of detectors before and after absorption can be seen to be proportional to the trapped component and hence the quantity of carbon and hydrogen in the original sample can be determined. The remaining component of the combustion products i.e. nitrogen, is measured with reference to pure helium carrier gas, the difference in thermal conductivity being proportional to nitrogen content. Detection is in the steady state and thus highly accurate and precise. Static systems have been proven to be highly reliable in 1000's of installations worldwide.

Figure 1: CHN Micro-analytical system (layout schematics)

Static system:



Dynamic system:

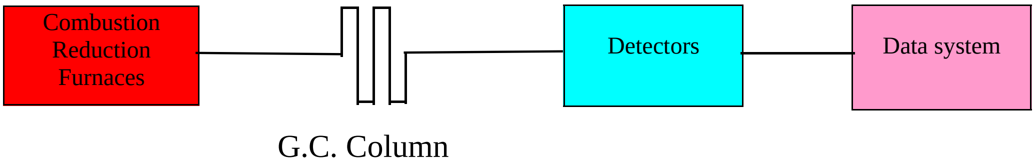


Figure 2: **CHN micro-analytical system – Trap Chemistry**

$$6\ H_2O + Mg\ (ClO_4)_2 \longrightarrow Mg\ (ClO_4)_2 \, . \, 6\ H_2O$$

$$CO_2 + 2\ NaOH \longrightarrow Na_2CO_3 + H_2O$$

The remaining nitrogen is referenced against pure helium.

Dynamic system

In a dynamic system the sample is dropped via gravity into the combustion tube at a predetermined time to meet with an oxygen enriched atmosphere. The mixture of combustion products (CO_2, H_2O and N_2) is then passed through a gas chromatographic column to separate the components resulting in a gas chromatogram of three peaks eluting in the order of N_2, CO_2 , and H_2O (Figure 1). In dynamic systems measurement is of the integrated area under an eluting gas chromatogram peak The subsequent signals are measured and referenced against compounds of known CHN content. Loss of precision can however occur in dynamic systems for reasons including samples with high hydrogen content often lead to tailing of the H_2O peak ; larger sample weights can give poor chromatographic separation (unresolved peaks) and gas chromatographic column efficiency decreases over time. By comparison in a static system the CO_2, H_2O and N_2 are determined by a simple linear voltage measurement of a steady signal that provides constant high precision.

The advantages and disadvantages of different instrument designs

Increasingly today analysts are looking for improved data accuracy, precision and long-term stability when determining CHN content to comply with more stringent quality practises. Currently there are three types of elemental analyser on the market, these are dynamic, hybrid and static measurement systems, all of which can be demonstrated to produce accurate and precise data. However, the consequences of these design differences start to show when the analysers are run in real laboratory environments.

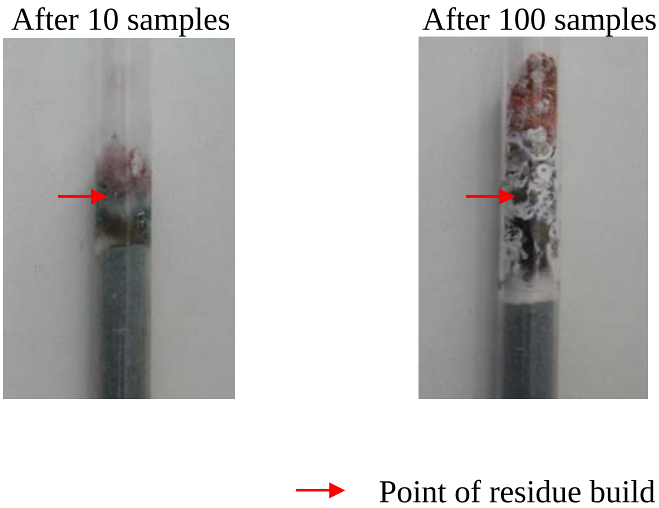
Combustion orientation

A notable design difference between the three types of systems is the orientation of the combustion furnace. While the static design has a horizontal combustion furnace, all the others operate with a vertical arrangement. The horizontal furnace arrangement enables the sample to be introduced into the combustion tube on a quartz ladle, which critically enables the removal of all sample residues after combustion. In a vertical furnace arrangement the samples are combusted on top of previously combusted samples. This difference is a major factor contributing to the advantages of a static system with a horizontal furnace over both the dynamic and hybrid designs.

When a laboratory undertakes to carry out a CHN analysis on a sample, 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. Consequently long-term stability is compromised and spurious results are likely to be generated due to memory effects from certain sample types. As the residue collects in the combustion tube (Figure 3) the flow characteristics of the combustion tube change, this change is particularly important when applying such changes to dynamic type systems as these systems depend on constant gas flow. Any changes in gas flow have a direct effect on calibration characteristics and stability.

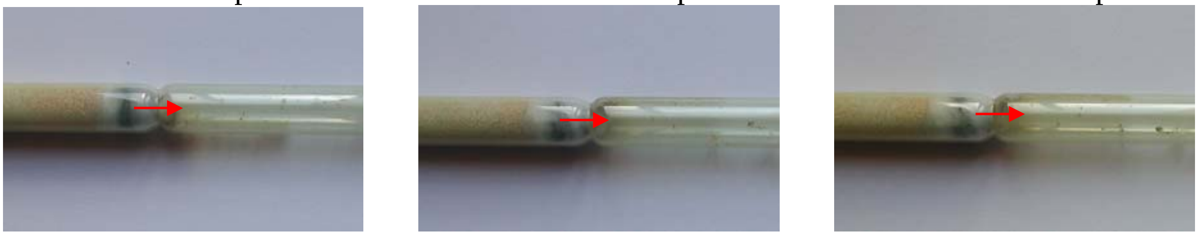
Figure 3: Effect of combustion tube orientation on residue build-up

Vertical furnace configuration


After 10 samples

After 100 samples

Horizontal Furnace configuration



After 10 samples After 100 samples After 1000 samples

→ Point of residue build up

The build of sample residue is a particularly 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 analysis. A common example of a slowly combustible material are the carbon fibres found in many modern day composite materials. The combustion of carbon fibres is not only a function of temperature but also of time. Vertical furnace analysers typically do not combust refractory type materials such as carbon fibres very well, because insufficient time exists in the dynamic 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 it is found in vertical systems that the blank values are elevated due to the sample that was left in the residue from the initial combustion now combusting along with the next sample, in this case a blank. The consequences for effects on sample data are obvious. In a horizontal furnace design memory effects such as the carbon fibres example above do not occur. Firstly, the residue is removed between the analysis of samples thus preventing memory effects. Secondly in horizontal systems such as the CE440 from Exeter Analytical[5], complete control over the combustion process enables the analyst to extend combustion time and oxygen flow to ensure total sample combustion.

Experimental and discussion

A series of experiments were carried out to test a commercial horizontal furnace elemental analyser, in this case an Exeter Analytical CE440, in the key areas that contribute to give operational benefit to the micro-analytical user.

* Accuracy and Precision
* Instrument stability
* Demanding sample types
* Ease of use.

Accuracy and precision

The most important criteria for CHN analysis in the majority of analytical laboratories are for optimal accuracy and precision across a wide range of sample types. With constant pressure to increase laboratory productivity an analyst does not want to set up their analyser with different operational parameters for every different sample type they come across.

In the UK, the independent Royal Society of Chemistry, MicroAnalytical Group regularly runs programs to study achievable data accuracy and precision on currently available micro-analytical instruments located in real working laboratories. Figure 4 shows a set of data, run on an Exeter Analytical CE440, used by the MicroAnalytical group as the benchmark for accuracy and precision testing.

Figure 4: Accuracy and precision (horizontal furnace design)

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

The test data in Figure 4 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 elemental analyser has been number one in terms of accuracy and precision in the last three independent Royal Society of Chemistry, MicroAnalytical group tests. In the last test the Exeter Analytical CE440 took positions 1, 2 & 3 in terms of best analytical data[6].

Instrument Stability

Nearly all commercially available microanalysis instruments can be demonstrated to give acceptable data accuracy and precision on selected samples. However, a truer reflection of the real data quality an analyst can expect in working laboratory conditions may be demonstrated in a longer-term stability test. Straying outside acceptable limits of data accuracy and precision not only can cause loss of data quality, but also can markedly increase the time spent in sample re-runs and recalibration.

To test the longer-term stability of the Exeter Analytical CE440 in real laboratory conditions, a run of samples were placed in the system and the calibration constants calculated. The calibration constant relates the number of microvolts detected to each microgram of element. A run of 60 samples (including 11 standards) were 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 5 run on the Exeter Analytical CE440 shows that all the calibration constants easily within meet these criteria.

Figure 5: Horizontal Furnace 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

Demanding sample types

Considerable variance in instrument 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 systems provide considerably better results with demanding samples. Another example of the benefits a horizontal system can offer is the ability to use rigid wall tin containers for the analysis of volatile liquids. With horizontal furnace analysers sample residue is removed between samples 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 even the most sensitive samples such as volatile liquids and air sensitive materials. The results in Figure 6 were derived from analysis of volatile fuel samples, the samples were sealed using a cold weld sealing device. The sample was analysed 10 times.

Figure 6: Attainable accuracy and precision on volatile samples.

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

Ease of Use

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

The Exeter Analytical Model CE440 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 to produce accurate C,H,N composition data on unknown samples is a broadly applicable and widely used technique. However this article demonstrates that results from CHN analysers of different design can vary considerably.

The Exeter Analytical Model CE440 has been demonstrated to routinely and simply produce accurate and precise data over long periods of time without system re-optimisation, thus saving time and expense to the micro-analyst. The examples above show how a horizontal furnace design for elemental microanalysis gives accurate and precise data, without the inherent problems associated with vertical furnace design systems.

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