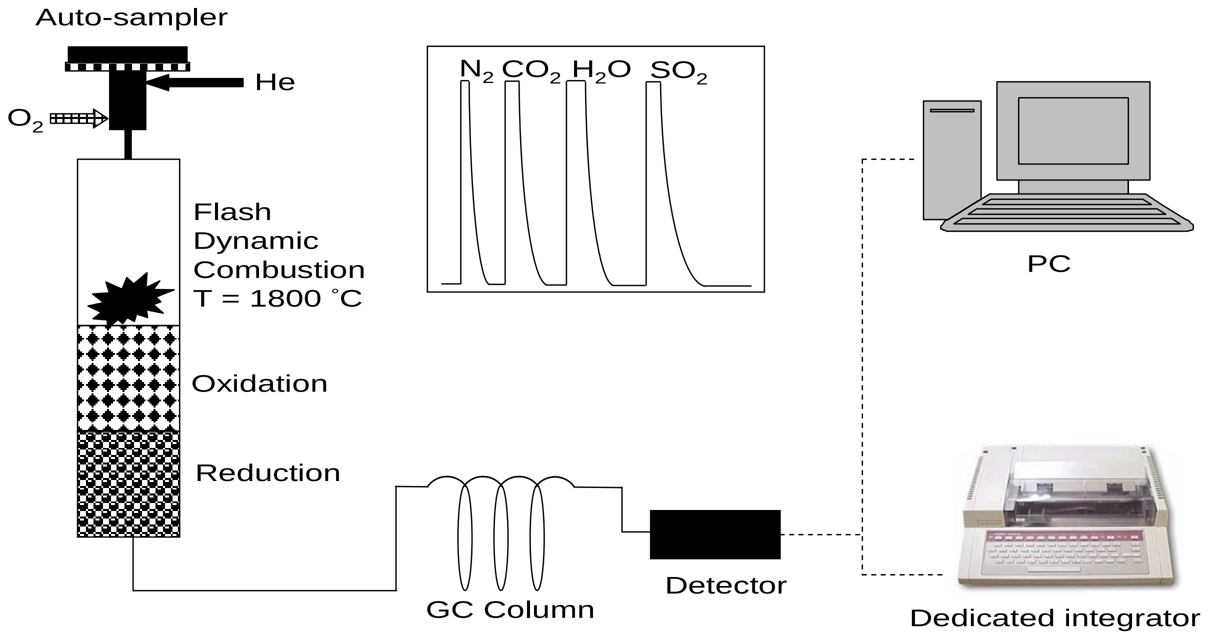
ISSN 1757- 5958

amc technical briefs

Editor: Michael Thompson Analytical Methods Committee AMCTB No 29 April 2008

CHNS Elemental Analysers



CHNS elemental analysers provide a means for the rapid determination of carbon, hydrogen, nitrogen and sulphur in organic matrices and other types of materials. They are capable of handling a wide variety of sample types, including solids, liquids, volatile and viscous samples, in the fields of pharmaceuticals, polymers, chemicals, environment, food and energy.

The analysers are often constructed in modular form such that they can be set up in a number of different configurations to determine, for example, CHN, CHNS, CNS or N depending on the application. This adaptability allows not only flexibility of operation but also the use of a wide range of sample weights from a fraction of a milligram to several grams (macro-systems.)

In its simplest form, simultaneous CHNS analysis requires high temperature combustion in an oxygen-rich environment and is based on the classical Pregl-Dumas method. This combustion can be carried out under both static conditions i.e. introduction of a set volume of oxygen or dynamic conditions i.e. a constant flow of oxygen for a set period of time. Often, catalysts are also added to the combustion tube in order to aid conversion.

Basic principles

In the combustion process (furnace at ca. 1000^{o}C), carbon is converted to carbon dioxide; hydrogen to water; nitrogen to nitrogen gas/ oxides of nitrogen and sulphur to sulphur dioxide. If other elements such as chlorine are present, they will also be converted to combustion products, such as hydrogen chloride. A variety of absorbents are used to remove these additional combustion products as well as some of the principal elements, sulphur for example, if no determination of these additional elements is required.

The combustion products are swept out of the combustion chamber by inert carrier gas such as helium and passed over heated (about 600^{o} C) high purity copper. This copper can be situated at the base of the combustion chamber or in a separate furnace. The function of this copper is to remove any oxygen not consumed in the initial combustion and to convert any oxides of nitrogen to nitrogen gas. The gases are then passed through the absorbent traps in order to leave only carbon dioxide, water, nitrogen and sulphur dioxide.

Detection of the gases can be carried out in a variety of ways including (i) a GC separation followed by quantification using thermal conductivity detection (ii) a partial separation by GC (‘frontal chromatography’) followed by thermal conductivity detection (CHN but not S) (iii) a series of separate infra-red and thermal conductivity cells for detection of individual compounds. Quantification of the elements requires calibration for each element by using high purity ‘micro-analytical standard’ compounds such as acetanilide and benzoic acid.

CHNS instrumentation

Combustion elemental analysers are manufactured in a variety of configurations to suit specific applications, and the choice will depend on the elements of interest, the sample type and size, and the concentration of the analyte.

All instruments require two gas supplies: (i) an inert carrier gas (helium recommended); and (ii) high purity oxygen (minimum 99.9995%). The strict specification for oxygen is associated with the need to reduce the nitrogen 'blank' contribution to an inconsequential level. Additionally, GC-type gas filters are also usually fitted to prevent trace organic species and water entering the combustion system.

The choice of sample introduction systems will depend on the application and the sample type. For solids or viscous liquids, samples are weighed out into tin capsules; for liquids, samples can be sealed in individual aluminium vials or introduced via a liquid auto-sampler. Both capsules and vials are pre-cleaned and dried to avoid trace contamination from oils and water acquired during their manufacture. Instruments are marketed with either simple 'one shot' introduction interfaces or a carousel type autosampler. In some instances a microbalance is directly interfaced with the analyser to allow the automatic recording of the weight of each test portion.

The combustion section of the analyser is designed to achieve both complete combustion of the sample and conversion of oxides of nitrogen to nitrogen gas (N_2). Although different approaches have been chosen by different manufacturers, the use of high purity copper is universal for the reduction stage. In some instruments, the combustion and reduction stages are housed in separate furnaces. In others, the reactions are combined in a single two-tier furnace. Catalysts are usually added to the combustion section to aid complete combustion and absorbents to remove potential contaminants. Both the catalysts/absorbents and copper metal are packed into readily exchangeable tubes made of ceramic material or high quality silica.

Instruments are classified as either 'static' or 'dynamic' in terms of their combustion characteristics. In the 'static' type, a pre-set volume of oxygen is added to the combustion tube before the sample is introduced. In the 'dynamic' type, the oxygen is added to the tube at the same time as the sample introduction and continues to flow for a set time. In the majority of applications, either method is applicable. For slow burning materials such as coals and cokes, where multiple additions of oxygen are required for complete combustion, the 'static' system is preferred.

The detection system within the analyser can take several forms depending on the combustion mode and sample size. With small test portions, the combustion gases can be separated on a GC column and quantified using a thermal conductivity detector. A schematic diagram of such a system is shown overleaf. If larger test portions are required, an instrument employing 'frontal' chromatography can be chosen. The latter approach employs a GC column with thermal conductivity detection but provides a step-wise profile for integration. Yet other detection approaches require no separation step but use separate infra-red and thermal conductivity cells to respond to individual elements.

Control of the instrument is established through a computer module, which is used to set up the program of work, report instrument diagnostics, and manage the calibration procedures.

Further considerations

The choice of instrument depends on a number of factors associated with the sample type. In instances where obtaining a homogeneous sample can prove difficult, food analysis for example, a greater weight of test material is required to provide a representative test portion. The larger the test portions and the higher the content of organic matter, the more oxygen will be needed to carry out the combustion successfully. This in turn means that larger capacity reduction tubes are needed to remove the excess oxygen and provide capacity for a reasonable number of combustions before replacement. For such applications, a macro-analyser would be required for gram-sized samples. For less heterogeneous samples, a micro-type analyser designed for milligram quantities would be appropriate.

Another important consideration is the amount of ash that is formed during the combustion and its removal. The ash will comprise the remains of tin and aluminium containers and the inorganic residues from the test portion. Instruments are manufactured with both vertical and horizontal furnace configurations. With vertical systems, ceramic crucibles are placed in the combustion tubes to accommodate the ash. This allows extended auto-sampler operation but can lead to back-pressure problems if the ash is not removed on a regular basis. In horizontal systems, the ash is removed after each combustion although this arrangement is difficult to automate.

Applications of CHNS Elemental Analysers

CHNS elemental analysers have been used in analytical laboratories for over thirty years. The method is used extensively across a wide range of applications, including pharmaceuticals, chemicals, oil-related products, catalysts and food. In the oil industry, an important application is the regular monitoring of coke build-up on refinery catalysts to ensure that regeneration procedures (involving controlled burning of the carbon) are executed at optimal intervals. Since many of these catalyst systems involve large quantities of noble metals such as platinum, palladium and rhenium, mismanagement of this testing would entail serious financial losses. In food analysis, the determination of nitrogen (as a surrogate for protein) is very important for pricing grain and evaluating meat products, and is increasingly undertaken by combustion analysis.

Further reading

The purchase of instrumentation requires a critical evaluation of a wide range of instrumental features in relation to the intended application and these are comprehensively addressed in a recent report of the Instrumental Criteria Subcommittee[1].An example of a test method covering CHN analysis of petroleum products and lubricants is also given[2].

References

(1)Instrumental Criteria Subcommittee (2005). Evaluation of Analytical Instrumentation – Part XIX: CHNS Elemental Analysers. (to be published)
(2)ASTM D5291 Instrumental determination of carbon; hydrogen and nitrogen in petroleum products and lubricants, test method for.

This technical brief was prepared for the Analytical Methods Committee by the Instrumental Criteria Sub-committee (Chairman Prof. S Greenfield)

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