

Industrial Gas Chromatographic Trace Analysis

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PREFACE

This book is concerned with the applications, potentialities and difficulties of gas chromatographic trace analysis in industry. This very specialized technique can only very briefly be included in courses on analytical chemistry at universities and technical colleges. Their primary consideration is to provide a broad education, and also the very expensive apparatus needed is generally not available for educational purposes. It is hoped that this book will serve as a guide to those who need to employ this analytical technique. Naturally, if a book of this scope is to be sufficiently informative it cannot encompass the whole field of gas chromatographic trace analysis. The following discourse is therefore based mainly on areas to which the author has himself contributed during many years of analytical research in the fields of petrochemistry and synthetic polymers. Even here such an extensive range of problems arises that the analytical chemist has difficulty in dealing with them in addition to his normal work. Consequently, new problems in trace analysis must be solved as quickly as possible, and developed into routine and, if possible, automated analytical procedures.

The work of the industrial analytical chemist is largely governed by economic and material objectives, and consequently often leaves too little opportunity for a detailed academic approach to the subject. Perhaps the reader will therefore bear with the author if some of the papers referred to are not discussed as extensively as he might consider necessary. This may appear unsatisfactory to those who have recently entered industry from technical colleges and universities. Nevertheless, they will soon recognize that this branch of physical analysis represents an important and often indispensable link between research and production, since gas chromatographic trace analysis assists in the development of new production techniques and in the improvement of existing methods. Moreover, the experience and knowledge gained frequently become part of the 'know-how' related to a process.

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H. Hachenberg

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PART 1

General Principles

1.1. THE TERM 'TRACE ANALYSIS'

Trace analysis means the determination of materials which are present in very low concentrations in pure substances, or in mixtures of substances, and which are generally referred to as trace components.

The field of trace analysis is frequently characterized by defining the limits of detection. Although this may be justified in many individual cases, generally speaking the scope of trace analysis cannot be defined absolutely. The definition of the range of concentrations depends largely on the particular problem in relation to the analytical methods available, and thus in practice it is relative.

This is especially true in the case of gas chromatographic trace analysis in which separation and determination of the individual components are carried out in one operation. Thus, it is frequently the case that the limit of detection is specified on the basis of a calculated sensitivity for the detector, or on an experimentally determined value for a definite group of substances.

Apart from the fact that uncertainties arise in comparisons of sensitivities between gas chromatographic detectors, the result of a gas chromatographic trace determination ultimately depends on many other parameters. Thus, for example, the efficiency of separation and its dependence on sample size, as well as the stability of the stationary phases on which difficult separations are carried out, are equally important factors. In addition to this, as in other methods of trace analysis, the composition of the material, the nature and state of the sample, the method by which it is collected, the material from which the sample container is made, and the location of the sampling point, etc. can all play a decisive role. For these reasons some theoretical limits of detection, which have been defined solely on the basis of the sensitivity of the detectors employed, cannot be achieved in practice. Special attention should be paid to this when drawing up specifications for high purity materials, since the best specification is useless if it cannot be validated because of an inadequate analytical technique.

In practice, a further important question concerns the requirements from a trace analysis and the concentration level at which it is meaningful to determine the trace components. In general, trace analyses will be necessary when industrial processes are endangered by corrosion and safety risks. Other

examples are the purity of monomers used in polymerization reactions where trace amounts of foreign substances can cause chain termination or branching, and the materials employed for catalytic processes where the active life of a catalyst is often determined by the trace constituents. Reference may also be made to the quality control of manufactured goods in which trace components can cause problems of discoloration, degradation or undesirable odours, or can give rise to health hazards. The analytical problems associated with atmospheric and water pollution should also be mentioned.

The term 'trace analysis' also depends on the requirements of the user and on the problem. Thus, for example, the determination of a component present at 100 ppm can be more important and far more difficult than that of another component present at 10 ppm or *vice versa*.

The analytical technique is itself undergoing continual development. Whereas 15 years ago a gas chromatographic analysis in the region of 0.1 % to 0.01 % was still considered to be very successful, it is now common, even in routine operation, to analyse in the range 10^{-4} % to 10^{-6} % and down to 10^{-7} % or less in special cases.

The results of gas chromatographic trace analyses are therefore no longer given as percentage concentrations but in ppm (parts per million) and ppb (parts per billion), where

$$1 \text{ ppm by weight} = 10^{-4} \text{ weight \% (weight/weight)}$$

$$1 \text{ volume ppm} = 10^{-4} \text{ volume \% (volume/volume)}$$

and

$$1 \text{ ppb by weight} = 10^{-7} \text{ weight \%}$$

$$1 \text{ volume ppb} = 10^{-7} \text{ volume \%}$$

1.2. AIMS OF GAS CHROMATOGRAPHIC TRACE ANALYSIS

In trace analysis, three basically different aims may be distinguished.

(a) Quantitative analysis of trace components of known identity.

In this case, the material to be analysed and the method are known. In addition to optimizing the conditions required for resolution on the gas chromatographic column and the operating conditions of the detector, it is of major importance that the calibration be correctly carried out. Careful attention must also be given to the noise level of the whole instrument, including the precision of the signal recorder and the associated limits of detection. Nowadays this kind of analysis is performed even with commercial gas chromatographs.

(b) Detection, identification and quantitative determination of specific trace materials in pure substances and mixtures of known substances.

Here the objective is well defined. The analysis is therefore relatively simple since the conditions under which resolution will occur, the choice of the detector and the sampling technique may be assessed on the basis of known parameters such as the chemical structure, polarity and boiling point of the trace component to be analysed. Measurement of retention times ensures a high probability of accurate identification in this instance.

(c) Detection, identification and quantitative determination of unknown trace components in materials of largely or completely unknown composition.

In this case, there is initially no information on the material to be analysed. It may, for example, involve the analysis of mixtures of products from new processes in which corrosion may take place, or of manufactured products in which discoloration, degradation and irritating odours can be detected. There are also difficult analytical problems associated with polymerization processes and in the examination of commercial samples.

The first task confronting the analyst is to isolate all the trace components and quantitatively estimate them as far as possible. Except in special cases, this can only be achieved by gas chromatography since it enables separation and measurement to be performed in one operation. In order effectively to distinguish all the trace components, the analyst must employ several different

polar columns in combination with universal and specific detectors. The use of a single column with only one detector is not sufficient and can lead to serious errors because important impurities can be overlooked owing to poor resolution or insensitive detection.

When it is considered that this problem has been solved, then identification of the trace constituents isolated must be confirmed since gas chromatography is generally a 'blind' technique. For materials present in trace amounts identification is the most difficult part of the analysis, and in spite of the many concentration techniques available, and also the capabilities of combined gas chromatography and mass spectrometry in the ppm region it can by no means always be achieved. Thus, in many cases it is not possible to completely analyse the trace components in unknown materials, but merely to indicate the presence of traces of unidentified compounds.

1.3. REQUIREMENTS FOR GAS CHROMATOGRAPHIC TRACE ANALYSIS

The first necessity for a gas chromatographic trace analysis is a sufficiently sensitive means of detecting components which have been separated. The method therefore depends primarily on the detector. If trace components are sufficiently well resolved from the other constituents, it is possible to increase the limit of detection by using larger samples. If this approach is not successful then there is little choice but to undertake time-consuming concentration procedures.

Before commencing a gas chromatographic trace analysis it is also necessary to consider the noise level of the whole instrument, as well as the best methods of sampling, sample injection and calibration. When this assessment has been made the crucial question of method of identification often still remains.

1.31. Detectors

The literature contains a large amount of information on detectors. Particular reference may be made to the publications of Lovelock, Gogh and Walker, and that of Halász in which an excellent survey and classification of the gas chromatographic detectors currently available is presented.¹⁻³ In the course of this book, for instructional purposes, detectors will be discussed in detail where they are applied to particular problems. The following sections therefore discuss only a few basic considerations from the author's own experience of the application of detectors to trace analysis.

Since the effort involved in trace analysis usually exceeds that for analyses in the percentage region, owing to the difficulty of calibration and the need for blank analyses, the linearity of the detector is not of such crucial importance as obtaining the highest possible selectivity and sensitivity with a noise level for the whole instrument as low as possible. The detector should also be largely insensitive to fluctuations in temperature, pressure and flow rate, and should be unaffected by contamination. Since in trace analysis the components to be determined are usually poorly resolved from the main constituents, the volume of the detector chamber should be small so as to minimize the amount of back-diffusion that can occur.

Excluding special cases, the following types of detector are employed for gas chromatographic trace analysis, which from a practical point of view may be characterized as below.

1.311. Non-specific detectors

THERMAL CONDUCTIVITY CELLS

Operated at low temperature and having the smallest possible detector volume.

Limit of detection: ~ 0.5 ppm for a gas sample size of 5 ml.

Response: Universal.

Applications: For materials to which the flame ionization detector (FID) does not respond; however, they are restricted to gases as a consequence of their low operating temperature.

Special considerations: Very sensitive to fluctuations in the temperature, flow rate and power supply.

HELIUM DETECTOR

Limit of detection: ~ 100 – 10 ppb for a gas sample size of 1 ml.

Response: Universal.

Applications: For all gases to which the FID does not respond, *i.e.* mainly inorganic and inert gases. An ideal supplement to the FID for the trace analysis of complex mixtures of gases.

Special considerations: The following difficulties result from the extremely high sensitivity: The quality of the gas sampling system must be of the highest standard. If it contains moving parts it must be provided with a helium purge to prevent the diffusing in of air. For the same reason, if traces of oxygen, nitrogen or carbon dioxide are to be measured, accurate sampling is possible only if special precautions are taken. A further difficult and time-consuming problem arises from the fact that the helium detector is just as sensitive to water vapour as to other substances. The water vapour taken in with each sample is concentrated in the column during the course of several analyses and after a certain time is eluted as a broad peak, causing the sensitivity of the detector to fall sharply and making further trace analysis impossible. Depending on the number of samples, their size, and their water vapour content, this problem occurs after about 6–8 hours, and in laboratory gas chromatographs it is overcome by prolonged heating. It is also necessary to keep the concentration of water vapour and other contaminants in the carrier gas as low as possible. The helium

employed is therefore purified by passing through a molecular sieve at liquid nitrogen temperature before it enters the gas chromatograph. Liquids cannot yet be analysed with this detector since, for the reasons already mentioned, normal sampling systems do not allow the use of a syringe injecting through a rubber septum. Unfortunately, only adsorption column packings such as activated charcoal, silica gel, aluminium oxide, molecular sieves or cross-linked polymers can be used since even a minute amount of column bleeding from a liquid stationary phase renders trace analysis impossible. Applications of the helium detector are therefore restricted to gases for the time being.

ARGON IONIZATION DETECTOR

Limit of detection: 100–500 ppb for a sample of 3–5 ml of gas or 0.01–0.02 ml of liquid.

Response: All substances having ionization energies below 11.6 eV.

Applications: Organic compounds. Trace amounts of inorganic and inert gases can only be determined under special operating conditions.

Special considerations: Sensitive to contaminants, water and column bleeding. The choice of stationary phase is therefore restricted.

RADIOFREQUENCY DISCHARGE DETECTOR

Limit of detection: ~100–500 ppb for a gas sample size of 5 ml.

Response: Universal.

Applications: Inorganic and inert gases, and gaseous saturated hydrocarbons.

It is a good supplement to the FID for the trace analysis of complex mixtures of gases.

Special considerations: Sensitive to contaminants and column bleeding.

Its applications are limited since polymerizable compounds easily form deposits on the walls of the detector and make it insensitive or temporarily unserviceable. It can therefore not be employed for the trace analysis of monomers. It is possible to destroy the polymeric film by having oxygen present.

1.312. Specific detectors

A distinction can be made between detectors which are specific for classes of substances and those which are specific for particular compounds. Strictly speaking only the mass spectrometer should be included among the latter.

FLAME IONIZATION DETECTOR (FID)

Limit of detection: ~10 ppb for a sample size of 2–3 ml of gas or 0.01–0.02 ml of liquid.

Response: All organic compounds except formaldehyde, formic acid and some perchlorinated hydrocarbons to which it responds with a very low sensitivity.

Applications: Universal use in the trace analysis of organic compounds which vaporize without decomposition. Trace analysis can be carried out on capillary columns if a good amplifier is used. Since it does not respond to inert gases and water, it is particularly suited to the analysis of traces of organic impurities in air and water.

Special considerations: Insensitive to fluctuations in temperature and carrier gas flow rate. It is therefore well suited to the routine analysis of trace amounts of materials. Sensitive to fluctuations in the flow rate and impurities in combustible gases: air (oxygen) and hydrogen. This is generally the most reliable detector for trace analysis.

ELECTRON CAPTURE DETECTOR (ECD)

Limit of detection: ppb region.

Response: Sensitive to substances having a high electron affinity such as halogen and nitro compounds, carbonyls and nitriles, organo-metallic compounds and substances with conjugated double bonds which contain aldehydic or ketonic groups within the conjugated system. No response to saturated hydrocarbons. Since the response is strongly dependent on the bond energy of the relevant hetero atom, very large differences in sensitivity occur between individual classes of compounds.

Applications: Specific detection of traces of substances in the groups mentioned above when present in mixtures of hydrocarbons or in air.

Special considerations: Sensitive to fluctuations in temperature, impurities in the carrier gas and from the column, and also to water when a tritium radiation source is used. The sensitivity under varying analytical conditions is often not particularly constant, nevertheless it is adequate for routine measurements. However, frequent calibration is necessary.

HALOGEN-PHOSPHORUS DETECTOR (HPD)

(Also called the alkali flame ionization detector (AFID) or the thermionic detector (TID).)

1.3. REQUIREMENTS FOR GAS CHROMATOGRAPHIC TRACE ANALYSIS 11

Limit of detection: This is generally based on parathion, of which 2×10^{-10} g can be detected. The limit of detection for halogen compounds can be given as 0.5–1 ppm for a sample size of 5 ml of gas or 0.02 ml of liquid, whilst that for phosphorus compounds is generally lower.

Applications: Specific detection of halogen and phosphorus compounds.

Special considerations: Very good specificity and reliable operation. However, some commercial models show a fall in sensitivity when first brought into use and only settle down after a number of hours.

COULOMETRIC DETECTOR (CMD)

Limit of detection: 1 ppm.

Applications: Specific detection of traces of sulphur and halogen compounds in mixtures of substances, particularly hydrocarbons.

Special considerations: Relatively difficult to operate since chemical reactions can take place before detection. It can only be used in the laboratory owing to the risk of breakage.

FLAME PHOTOMETRIC DETECTOR (FPD)

Limit of detection: ~ 100 ppb for a sample of about 5 ml of gas or about 0.03 ml of liquid.

Applications: Specific detection of sulphur and phosphorus in mixtures of substances.

Special considerations: Good stability, simple operation. Complications arise owing to quenching effects if trace components are masked by those present in concentrations at the percentage level.

ATOMIC ABSORPTION (AAS)

Limit of detection: ppb region.

Applications: metallic compounds in gases and liquids.

MASS SPECTROMETER

Limit of detection: When used in combination with a direct ion source and suitable capillary columns, about 10 ppm (measured as hydrocarbons) gives a mass spectrum which can still clearly be interpreted.

Response: Universal.

Applications: All substances which can be eluted by gas chromatography.

Special considerations: An efficient differential pumping system is required for trace analysis. Interpretation at the ppm level becomes difficult, or impossible, if the component concerned does not show a peak for the parent molecule.