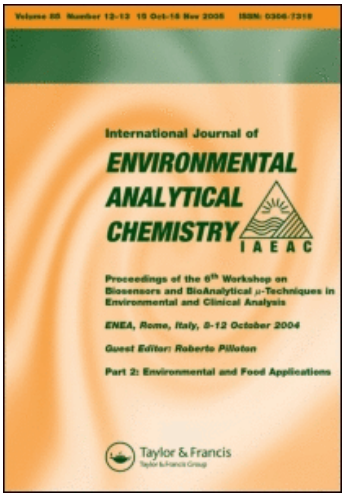

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Modern Analytical Methods for Monitoring Workplace Atmospheres

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Modern Analytical Methods for Monitoring Workplace Atmospheres†

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Since measurements of exposure to hazardous substances were made obligatory in Germany under the Hazardous Material Regulation and Regulations for Accident Prevention there has been a need for widely-applicable, economic methods for determining airborne organic substance concentrations at workplaces. The relevant limits, which are based on toxicological and industrial hygiene data, are drawn up annually by the German Science Foundation and published as "Technische Regel für gefährliche Arbeitsstoffe" (TRgA 900) by the Ministry of Employment and Welfare.

Most organic substances, that have been assigned limits can be determined by gas liquid chromatography. The system described here is based on multicomponent GLC analysis. It has been used at BASF, the chemical-manufacturing company, where since 1979 approximately fifteen thousand workplaces have been evaluated. Hazardous substances have been detected at levels down to a few micrograms per cubic meter.

The standard system encompasses:

—personal air samplers operating for 8 h;
—adsorption by a solid sorbent;
—desorption by solvent;
—simultaneous GLC-separation on two different capillary columns;
—computer correlation of the qualitative and quantitative data of the two chromatograms (plausibility check);

†Dedicated to Professor Carl-August Wetjen on the occasion of his 60th birthday.

Presented at the 14th Annual Symposium on the Analytical Chemistry of Pollutants, Barcelona, November 21–23, 1984.

—automatic print-out of the analytical report;
—transfer of the results to a data bank for documentation.

Details are given of the method involving adsorption on activated charcoal and desorption with carbon disulfide. Benefits, cost advantages, and limitations are discussed.

Special sampling by means of other adsorbents (e.g. silica gel) in conjunction with special desorption, formation of derivatives, headspace analysis, and adsorption by liquids are techniques used to supplement the standard method of organic trace analysis in the field of industrial hygiene.

KEY WORDS: Industrial hygiene, ambient air, multidimensional gas-chromatography, electronic data processing, workplace monitoring.

INTRODUCTION

In the industrial nations of the West, more and more attention is being devoted to safeguarding human health by the enactment of guidelines and ordinances on the maximum concentration of hazardous substances that can be permitted in the workplace.

In the Federal Republic of Germany, these permissible limits (referred to as the "Maximale Arbeitsplatzkonzentration" or MAK value for short) are laid down by the "Senatskommission der Deutschen Forschungsgemeinschaft" (DFG)[1] in the light of the available knowledge in occupational medicine and toxicology. These values represent the average concentrations of the individual substances that can be tolerated over an eight-hour exposure period.

At the present time, acceptable figures from the human toxicological aspect cannot be quoted for the maximum permissible concentration of carcinogens. In this case, control limits referred to as "Technische Richtkonzentrationen" (TRK values) are laid down.

The West German MAK/TRK lists currently contains 360 substances. Of these, 250 are organic substances that, owing to their comparatively high vapour pressure, predominantly occur in the form of gases or vapours in the air in the workplace. The lists also include substances that may be present in the workroom air in dust form.

In all production plants in which these hazardous substances are handled, the employer is obliged by law, i.e. the West German "Arbeitsstoffverordnung", the Unfallverhütungsvorschrift and the associated regulatory statutes, to perform routine measurements in order to check that the limits are not exceeded.

ANALYTICAL METHODS ADOPTED IN BASF FOR INDUSTRIAL SAFETY

Problems

In the heavy chemical industry the analytical problems relating to industrial safety are governed by the following factors:

1) In view of the multiplicity of products manufactured and processed, the analytical programme must include a very large number of industrial substances. This not only implies that an analytical method must be available for each substance to which a control limit is attached but also that the method concerned must not be disturbed by the presence of other substances, whether or not they too have a control limit. This applies particularly to large concerns in which different production units closely adjoin one another in the interests of integration.[2] Under these circumstances, industrial materials from the one factory may well be present in the air of neighbouring factories.

2) In modern chemical production plants, the operations are seldom confined to one workplace. For this reason, stationary methods of measurement can be ruled out for monitoring the actual exposure conditions. Owing to the differences between the various operations in the individual parts of a production unit, it is frequently impossible to find a few workers whose tasks can be taken to be sufficiently representative to allow measurements from which conclusions can be drawn on a large number of operators. It follows from this that an extremely large number of samples must be examined.

At the present time, the total number of employees engaged at BASF in Ludwigshafen is 50,000, and 35,000 of these handle hazardous materials. For this large complex, we have developed a system that satisfies the analytical requirements involved in industrial safety and also permits rationalized analysis of large numbers of samples of widely different natures and with big differences in the number of the constituent substances to be determined. In presenting our concept for this, we shall restrict ourselves to organic industrial materials.

Sampling

The majority of organic industrial materials to which a MAK/TRK control limit has been assigned have sufficiently high vapour pressures to allow determination by gas chromatography. Since the limiting values in many cases are of the order of a few ppm, the airborne substances must be enriched. This requirement for a cumulative sample also arises from the definition of the control limit as the average concentration over a period of 8 hours.

As has already been stated, stationary sampling does not yield any relevant information on the actual exposure conditions for the individual operators. Consequently, all samples for industrial safety measurements are drawn by a battery-operated suction pump weighing about 200 grammes. It is carried about in an overall pocket and draws about 20–40 litres of air through a collector in a period of 8 hours. The type of collector depends on the nature of the substances to be investigated, but we shall deal with this in more detail later.

We have tested some of the passive collector systems that have recently been offered by various manufacturers, but we have decided to adhere to active collectors for the following reasons:

1) Manufacturers of diffusion collectors quote conversion factors for many substances in order to allow the imaginary sampling volume to be calculated. The lists of factors that they draw up are usually incomplete and contain only those substances for which a control limit has been laid down. However, we wish to determine, whenever possible, all the substances present in the workroom air, including those for which no binding limit yet exists. In these cases, we must determine the conversion factors ourselves by time consuming procedures. In addition to this the experience gained up to now is not sufficient to permit the imaginary sampling volume in multicomponent systems to be calculated. As opposed to this, the concentration of unknown substances can be estimated by active sampling.

2) As will be discussed in detail later, we use different types of collecting media, some of which are not or not yet available as diffusion samplers. Consequently, the active system is much more flexible for our purposes.

3) In contrast to diffusion collectors, active sampling also embraces particulate airborne substances.

In the light of the experience that we have gained up to now, the only recognizable disadvantage of active sampling is that a battery-operated pump has to be carried, but the workers being sampled do not consider this to be inconvenient.

Beside active personal air-sampling the second fundamental principle in our measuring concept is simultaneous multicomponent analysis. In view of the extent of the samples that we have to deal with and the large number of substances to be analysed, it is impossible to determine each individual by separate methods. Thus the analytical techniques described in the literature for industrial safety measurements on individual substances, e.g. NIOSH, can act only as a guide in the development of our own methods. Obviously no one method can apply to all the substances concerned, but we endeavour to achieve our aims with the minimum of methods and processes.

Another requirement that defines our target is that the entire analysis must be automated as much as possible. Automation must embrace the measurement itself and the evaluation and extends to the compilation of the final analytical report. Considerable assistance in this direction is given by data processing, which we use not only to record and process signals from the measurements but also to control the analytical apparatus.

The rationalised procedure allows a large flow of samples to be dealt with and thus routine health surveillance of a representative section of all employees. By this means, statistically significant data can be obtained for occupational medicine and epidemiological studies.

Workplace monitoring program

Sampling is organized by the Safety Department,[2] whose staff determine the nature of the industrial materials that are being handled by discussing the entire situation with the Production Department. Whenever necessary, the analyst also participates in these discussions. The Safety Department give instruction in operating the sampling system. Whenever possible, workers are

selected who are considered to be exposed to conditions that are typical for those relating to an entire group of operators.

From the list of expected substances that has thus been compiled, the analyst responsible decides how samples have to be taken (if necessary in more ways than one) and whether an analytical method exists for all the substances to be determined.

During sampling the operator fills out a job description listing the work done and time spent at each work station. The substances handled are also noted. The results of the study are taken into account by the Safety Department in compiling the industrial safety register from the analytical values determined.

Standard method

The majority of the industrial materials that we are concerned with can be analysed by a capillary gas chromatographic method that we have devised. By virtue of its versatility, it shall be referred to as the "standard method" in the further course of this paper. Special methods, which we shall deal with briefly later, are resorted to for substances that cannot be determined by the "standard method".

The standard method consists of collecting a sample on activated charcoal, subsequent desorption by carbon disulfide and determination by simultaneous capillary gas chromatography with two separation systems of different polarity. The sampler pump draws air at a rate of 20–40 litres in 8 hours through a tube filled with 150 mg of activated charcoal. The substances thus collected are desorbed with 1 ml of carbon disulfide, to which tetradecane is mixed as an internal standard for the subsequent gas chromatographic determination. Limits of detectability of the order of a few ppb, expressed in terms of the concentration of the substance concerned in air, can be obtained if 1–2 microlitres of the carbon disulphide solution is injected into a chromatograph with a flame ionization detector. Since there are very few industrial materials with a MAK/TRK value of less than 1 ppm, the limits of detectability involve a safety factor of at least 10 but usually more than 100. Consequently we can reliably detect in most cases concentrations that are only a few percent of the control limit. At this stage, we can safely say that the overwhelming majority of the results obtained in our measurements lie within this range of

concentrations. It is only in very few cases that the limit values are exceeded.

The capacity of the sampling system has been primarily designed for the low ppm range. It is inadequate for higher concentrations, which need not necessarily entail transgression of the limits; for instance, the MAK value for acetone is 1,000 ppm = 2.4 g/m^3. In cases of this nature, either a larger quantity of activated charcoal, e.g. 1 g, or a smaller sample must be taken. In practice, however, such high concentrations are unrealistic and have not yet occurred in the BASF monitoring programme.

If any new substance is to be included in our measuring programme, whether or not a control limit has been assigned to it, the first step is to check whether the "standard method" of determination can be applied to it. For this purpose, the following questions must be clarified beforehand.

1. Can the substance be determined direct by gas chromatography?
2. Can a sample be adsorbed on activated charcoal? If so,
3. What is the recovery rate with respect to the concentration if the desorption solvent is carbon disulfide?
4. Is the recovery rate reduced if the adsorbed sample is stored for a certain length of time?
5. Does the solution of the desorbed sample in carbon disulfide remain stable for at least 20 hours?

Hence, not only do we check whether the method is suitable in principle (items 1–3) but also whether it can be applied under practical conditions (items 4 and 5). If it turns out that the adsorbed sample undergoes a change within the course of a brief period or that the concentration of the solution does not remain constant after desorption, restrictions are imposed on the method's scope. In other words, the method cannot be adopted unless it is certain that the sample cannot be analysed immediately after sampling. This would not be the case if the samples were taken in a remote subsidiary, and not on the BASF Ludwigshafen site, and sent by mail to BASF.

The sample could always undergo a change after desorption if substances were collected that react either with one another or with the carbon disulfide. In this respect, allowance must be made for

the fact that the carbon disulfide is not added until the entire contents of the activated charcoal tube have been transferred into the flask of an automatic gas chromatograph sampler. Under these conditions, the catalytic action of the activated charcoal remaining in the solution may accelerate reactions that normally proceed only very slowly. For instance, lower alcohols react with carbon disulphide to form the corresponding xanthates; and primary amines to form isothiocyanantes. In the latter case (Figure 1) the reaction is completed within a short time, with the result that many primary amines can be determined in the form of their derivatives. As opposed to this, the formation of methyl xanthate is simply a disturbing side reaction that always detracts from the accurate determination of methanol if the desorbed sample were to be allowed to stand for more than 10 hours before it were measured. An example of where this would apply is given by samples that are measured overnight with the aid of an automatic sampler.

Apart from the substances just mentioned, there are many others that, although they can be concentrated on activated charcoal, either

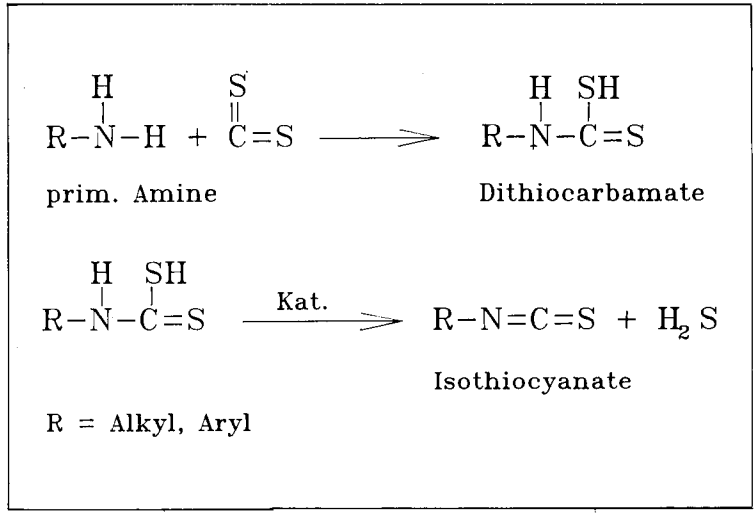

FIGURE 1 Derivatizing desorption.

cannot be desorbed quantitatively with carbon disulphide or enter into undesired reactions with this solvent. In cases of this nature, resort is taken either to other desorption solvents or to other sampling systems. We will discuss these methods in detail later on.

In the preliminary examination to determine recovery rates, the substances concerned are injected direct into the tube of activated charcoal. Afterwards, the tube is sealed and kept for 24 hours at room temperature. In this equilibration time, the vapours of the substances are distributed over the activated charcoal. By means of a comprehensive series of tests with gases in varying defined concentrations, we have convincingly proved that the results obtained on all model substances investigated by the substantially more simple injection techniques that we adopt agree well with those obtained by direct adsorption from the gas phase.

The preparatory work that has been described has been performed on each individual substance that is relevant for our purposes; at the present time there are about 120 substances with control limits and about 200 substances to which no control limit has been assigned but which are handled in our production units and laboratories.

It is evident from the very number of likely compounds that we must rely on chromatographic systems with a high separation efficiency in an analysis involving the simultaneous determination of many components. Consequently, high-performance capillary columns are absolutely essential for the gas chromatography. Nevertheless, the possibility cannot be excluded that, in a complex mixture such as the air sample represented in the chromatogram (Figure 2), the signals overlap or peak identification by the computer is incorrect.

On the other hand, the large number of samples involved does not allow the identity of each peak in a chromatogram to be critically checked by a trained observer and, if necessary, verified, e.g. by recording and comparing the mass spectrum with the aid of the GC/MS. Thus we have developed a method that permits automated plausibility control of the qualitative and quantitative results. It consists of simultaneous gas chromatographic separation on two capillary columns of different polarity and subsequent evaluation and correlation of the results with the aid of a laboratory data system.

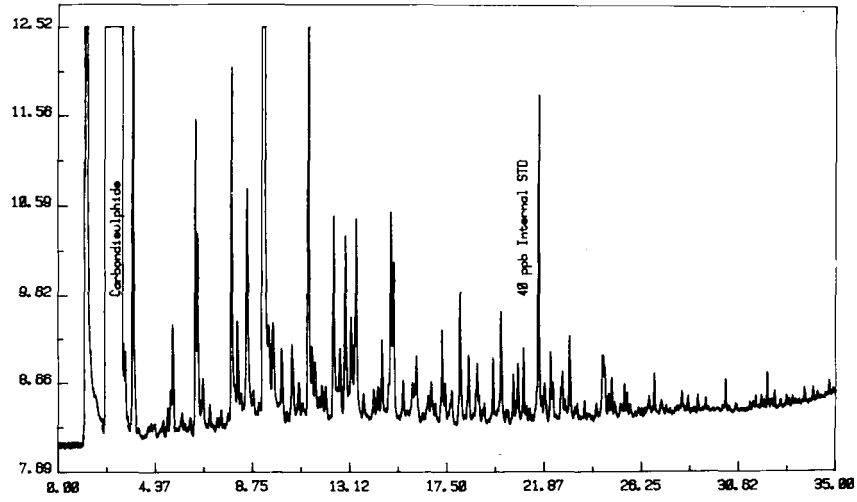

FIGURE 2 Chromatogram of an air sample.

Although a double capillary gas chromatograph system of this nature has already been described a number of times in the literature,[3] we believe that we are one of the few laboratories in which this method has been adopted on a large scale for routine measurements. For this reason, we wish to go into more detail on the technique and the experience that we have gained with it.

The principle underlying the method is shown by the schematic diagram in Figure 3. The injected sample is split into two columns within the GC-injector. The geometry of the splitter ensures that the capillaries extend equally into the injector space and do not contact the wall of the glass liner or one another. Thus no discrimination effects can occur in any one of the two systems. Now that high-performance fused silica capillaries of very good quality can be obtained and since there is a wide selection of stationary phases on the market, we use this type exclusively because of the ease in handling.

Great significance is attached to the selection of the stationary phase for the separation of complex mixtures of substances. The selection of a suitable pair of capillaries is of decisive importance. On the one hand, both should have different separation characteristics. On the other hand, the probability should not arise that the one

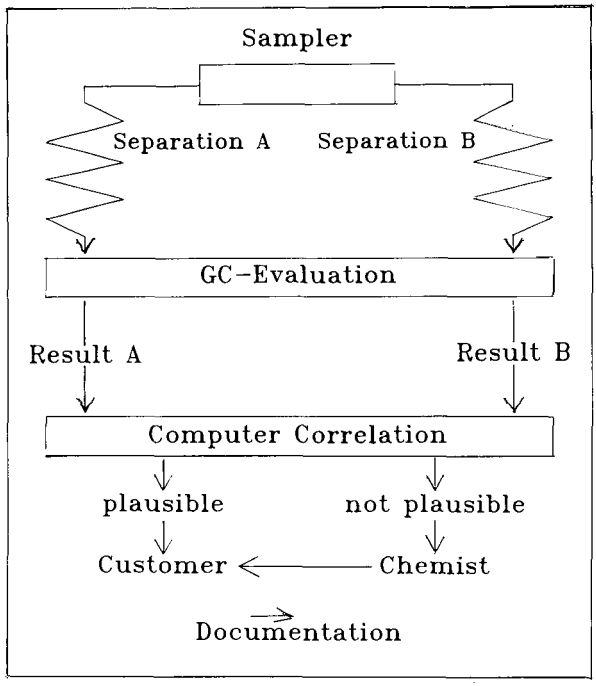

FIGURE 3 Flow diagram of computer controlled double capillary gas chromatography.

substance superimposed on one system could be disturbed on the other system by another substance.

Our experience shows that a combination of columns with extremely different properties, e.g. nonpolar, methylsilicone phases with polar polyethylene glycol phases, is often less likely to achieve this goal than a combination of columns with only comparatively slight differences in separation properties, e.g. the silicone phases SE 54 and DB 1701. For this reason, we prefer to combine stationary phases of medium polarity. It is important that the columns have similar geometry, i.e. the same length and inner diameter, so that the sample is evenly divided between the two separation systems.

Another point to observe is that both capillaries should have similar adsorptivity towards polar substances. The aim of this

measure is to avoid that substances display pronounced tailing on one of the two systems and symmetrical peaks on the other. Under these circumstances, integration could give rise to different values for the areas of the peaks, and the amounts involved may affect the retention times. As a consequence, the automatic correlation would lead to false results.

The range of substances that we have to analyse ranges from very volatile materials, e.g. diethylether, to others with a comparatively high boiling point, e.g. diphenyl (Bp. 254°C). Consequently, we are forced to commence our temperature programme at as low an initial value as possible. This also imposes a limitation on the combination of various capillaries, because the adaptibility of the entire system is restricted if the ranges of operating temperatures do not coincide. For the same reason, a few highly polar stationary phases, e.g. Carbowax 20M can be used only if the operating temperature does not have to be below 60°C and if the advantage of a high final temperature can be dispensed with.

In order to obtain the highest possible k'-values for volatile substances as well, we prefer columns with the lowest possible phase ratio. Capillary columns with a film thickness of 1 micrometre, an inner diameter of 0.25 mm, and a length of 25–30 m have a sufficiently small phase ratio for separating volatile substances, in which case the lower operating temperature should be at least 40°C.

An example is shown in Figure 4, in which can be seen the two chromatograms obtained from a test sample in double capillary gas chromatography. By no means do all of our samples have such a complex composition as shown in Figure 2. Nevertheless, the example clearly reveals that manual evaluation, i.e. correlating the results obtained in each chromatogram, would be too involved and tedious. In practice, the only method of coping with the task is to resort to a data processing system. This is precisely the advantage of the simultaneous double capillary technique, namely largely automated plausibility control of the qualitative and quantitative chromatographic data.

With the aid of a program that has been specially developed for the laboratory data system (Figure 5), it is determined whether a substance peak corresponding to the retention times for the reference substance can be found in both separation systems. If the peak has emerged, it is checked whether the calculated concentrations agree to

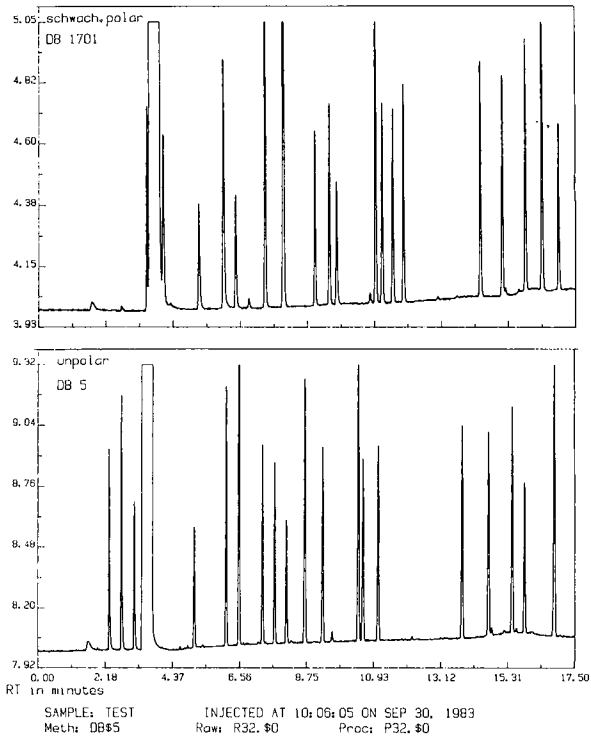

FIGURE 4 Simultaneous chromatogram.

within a given range of error. If they do not agree satisfactorily, the larger value is discarded, because another component has evidently been superimposed on the peak in the separation system concerned. If the calculated values for the concentration differ only slightly from one another, the mean is taken as the final result. Peaks that cannot be identified from their retention times are rejected in each separation system; if their magnitude is significant for industrial safety, they are subsequently identified by GC/MS.

In practice, the procedure described here is not quite so simple as it sounds. The main reason for this is that, even with the most modern GC techniques, difficulties always arise in keeping the retention times constant within a narrow time window over a long period of time. But it is precisely this requirement that counts,

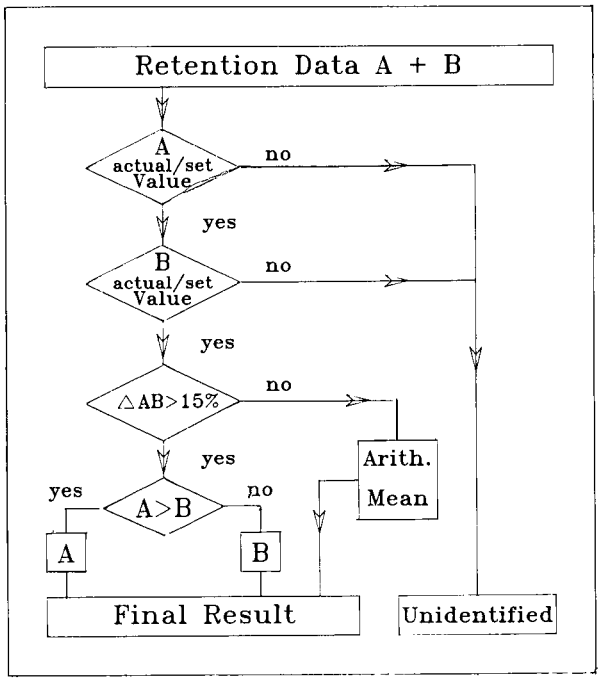

FIGURE 5 Flow diagram of chromatogram data correlation.

because utmost efficiency in computer-assisted double capillary gas chromatography preliminarily depends on the existence of an extensive set of retention time data that will remain valid for a long period of time.

Another necessity besides the consistency of GC parameters is the stability of the capillaries themselves, because changes in adsorptivity, and on the acidity of the support in particular, act selectively on only certain compounds, whereas others are not affected. Consequently, the properties of the separation system must be regularly checked. For this purpose, we have prepared four to five test mixtures, each containing 40–50 substances that can be readily separated on both capillaries with a multi-stage standard

temperature programme. These tests allow the reference retention times to be controlled at regular intervals, and it is left to the discretion of the operator whether any correction is required. By this means, the data file always contains an up-to-date set of retention times for about 250 substances on two separation systems. The data system "automatically" classifies a substance in the light of this file. As a result, manual evaluation is restricted to the few exceptional cases in which identification is not feasible.

Difficulties in identification frequently occur if substances are eluted in large amounts, with the result that the column capacity is overloaded and the retention times are shifted. For this reason, too, preference should be given to capillaries with the smallest possible phase ratio, i.e. largest film thickness.

In some parts of a chromatogram, particularly those that cover the range of volatile substances, the peaks follow one another in very close sequence. On account of this, the time window that is used for identification should be as narrow as possible. On the other hand, it must not be so small that the concentration-dependent fluctuations mentioned above cannot be recorded. The experience that we have gained up to now indicates that a window size of ± 0.02 minutes is necessary for positive identification in both windows.

The automated GC-method described is particularly suitable for the economical analysis of large numbers of samples in which only a small series of similar composition occur, as is very frequently the case in analysis for industrial safety. In the "standard method" described here, the work of the laboratory staff is essentially reduced to feeding the automatic sampler, feeding the sample sequences at the computer terminal, and monitoring and maintaining the retention time data files. The entire analyses themselves including 24-hour control of the instruments is supervised by the laboratory data system. The majority of the substances handled in our production units can be determined by means of this standard method.

Modifications of the standard method

Despite the fact that many industrial materials can be sampled on activated charcoal, for some substances carbon disulfide is an unsuitable solvent for desorption. The reason for this is that it either reacts with the sample, e.g. primary amines, or does not desorb

sufficiently. In cases of this nature, we employ other, usually polar solvents or solvent blends. For instance, if the solvent blend consists of dichloromethane and methanol, much better recovery rates are achieved with ethylene chlorohydrin, phenol and glycol ethers than with carbon disulphide. In this case, however, it must be accepted that the solvent peak is very much wider than that for carbon disulphide and could thus prove very troublesome and mask peaks of some important components.

In the analysis of some reactive substances, the "standard method" cannot be applied unless allowance is made for the period of time elapsing between sampling and analysis. If the sample contains epichlorohydrin, it must be analysed immediately after sampling. Although adsorbed styrene can remain stable for some time, it reacts comparatively rapidly after it has been desorbed in the form of a solution, with the result that the measurement must be performed within a few hours. This procedure must be initiated by the operator himself and can thus be considered a modification of the "standard method".

Other modifications are introduced by substituting selective GC detectors, e.g. thermionic detectors, for the determination of nitrogenous compounds, instead of flame ionisation detectors. In this form, however, the method is mainly applied for individual substances, e.g., acrylonitrile, and it is thus regarded as an entirely different analytical method.

Different analytical methods

The analytical methods falling under this category differ essentially from the standard method either in the procedure for sampling or for the determination itself. The fact that a different GC detector is used has already been mentioned. The simplest variation besides this is that the capacity of the sampling system has been increased. This is necessary if substances with a high volatility or a low break-through volume have to be collected. The need may also arise if the adsorbent's capacity for a substance with a high control limit were to be exceeded in the one individual case, with the result that remeasurement would be required; but cases of this nature hardly ever occur in practice.

Some substances that can be sampled with the standard activated

charcoal tube necessitate changes in the methods of desorption and determination. For instance, vinyl chloride and butadiene are desorbed with benzyl alcohol and kept at a controlled temperature in a closed vessel. After equilibrium has been attained, the determination is made from the gas phase in the sample bottle by means of headspace gas chromatography.[4]

This injection technique is also adopted for the determination of secondary and tertiary amines, in which case the selectivity is improved by means of a nitrogen thermionic detector (N-FID). The sample is taken by adsorbing the substances in an acidic aqueous solution in a leakproof miniature impinger. The sample is rendered alkaline, and kept at a constant temperature of 80°C in a closed vessel until equilibrium has been attained. The amines are determined from the gas phase. A feature of this method is that a small amount of ammonia is mixed with the carrier gas in order to reduce the capillary column's adsorptivity for basic substances (Figure 6).

Likewise, acidic substances, e.g. phenols and organic acids are absorbed in aqueous alkaline solutions in a mini-impinger. Before gas chromatography, these substances must be converted into their

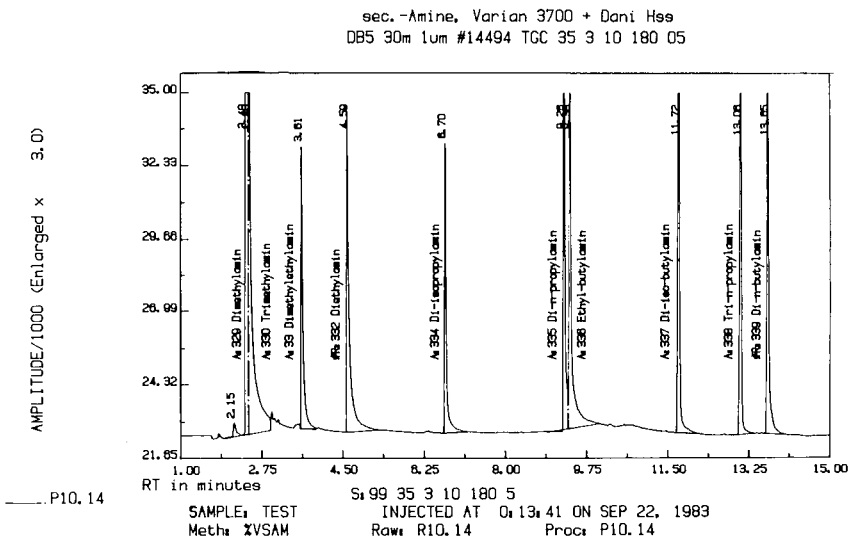

FIGURE 6 Headspace GC of amines.

derivatives in the aqueous solution. Examples of reagents that are suitable for this purpose in individual cases but by no means in all are diazomethane and pentafluorobenzyl bromide. In some cases, the gas chromatography determination of the derivatized substances can be performed direct from the aqueous solution by headspace techniques in analogy to the method adopted for secondary and tertiary amines. If the derivatives' volatility is too low for a determination of this nature, the sample must be prepared by extraction.

Since only small volumes are concerned, sample preparation is quite simple using a small extractor developed by Cais and Shimoni. Owing to the manual work involved in separating the phases, this technique is being adopted on only a temporary basis until a more sophisticated method is devised. The main technique that can be considered is high-pressure liquid chromatography. At the present time, our laboratory is working on analytical methods of this nature, in which the labour-intensive and only partially automatable derivatization can be dispensed with.

Derivatization is also resorted to for the determination of formaldehyde and other aldehydes, but in this case it does not involve much outlay. The aldehydes react with benzylethanolamine to form benzyloxazolidines on a polymeric solid support coated with the reagent.

In the derivatization method[5] adopted for dialdehydes, e.g. glutaraldehyde, the derivatives are absorbed in a solution of 2,4-dinitrophenylhydrazine in a miniature impinger. The determination is performed direct from the solution by HPLC with UV-detection at 350 nm. In this case, the control limit is 0.2 ppm and the limit of detectibility is 0.01 ppm, and these figures can be determined with adequate reliability.

In order to rationalise our efforts in dealing with a large number of samples, we resort to derivatization reactions only in such simple forms. In the determination of formic acid, we prefer absorbing the sample in alkaline aqueous solution followed by ion-exchange chromatography instead of using derivatization.

For the determination of some polar substances, the adsorbent that we use in the sampler tubes is silica gel, which has a low adsorption capacity for nonpolar substances. Thus this method of sampling also entails preliminary removal of disturbing substances.

Either nonpolar or polar solvents, depending on the nature of the components to be determined, can be used for desorption. For instance, substituted pyrrolidones can be desorbed at very good recovery rates by a 90:5:5 mixture of methanol, isopropanol and water.

Finally there is a group of substances whose sorption characteristics do not allow samples to be concentrated either by adsorption or absorption. It includes some gaseous substances, e.g. Frigens and methyl chloride, and very volatile compounds, e.g. dimethylether. In these cases, practically the only method that can be considered is gas sampling. A system has been developed for obtaining a representative sample for an eight-hour shift. It consists of an evacuated glass vessel into which air is slowly introduced through a very narrow opening.

After the sample has been taken, the degree of vacuum still remaining in the vessel is measured and the constituent air is subjected direct to gas chromatography.

Up to now, we have dealt with industrial substances that can be present in the air in the form of vapours. There are others that have such a low vapour pressure that practically the only exposure hazard that they present in the workplace is by inhalation of a fine dust. In these cases, we again resort to active sampling. The large particles of dust that do not enter the lungs are determined separately by means of a minicyclone, type Cassella, London. The dust particles collected are removed from the filter with a solvent, and they are usually analysed by HPLC, because the substances concerned have, as a rule, very low vapour pressures. Provided that a chromophore is available for UV-detection, the sensitivity is completely adequate, because the total volume of air involved in sampling is one cubic metre and many substances can be reliably detected in concentrations of a few microgrammes per cubic metre. Measurements of this nature are frequently performed on substances that have not yet been included in the MAK/TRK lists but might be presumed to represent a potential hazard; examples are crop protection agents.

SUMMARY AND CONCLUSIONS

We have attempted to provide an insight into the analytical methods

that we have adopted to further occupational safety. In doing so, we have restricted the scope of the paper to organic substances. By means of the instrument that we have described, we can currently determine on a routine basis 123 of the 140 substances in the West German MAK/TRK list that may be encountered on our industrial site and all the substances that have a TRK value. In addition, we record a large number of other substances for which no control limit has yet been laid down. The total number of substances for which we have devised a routine analytical method is at present about 250 and is continually being increased. In all cases in which unknown substances are detected in significant concentrations in a sample, their identity is established by coupling gas chromatography with mass spectroscopy. In some cases there are intermediate products or in many cases rarely used solvents. These substances, too, are quantified, so that exposure data can be presented at a later date if required for new studies in occupational medicine.

Ever since 1979, we have examined about 15,000 samples by the analytical methods described and, in doing so, have continuously improved and rationalised our techniques. At the present time, the number of highly qualified technicians required to perform the continuous control measurements is two to three, depending on the nature and number of the sample taken.

All the methods adopted must be available at all times, and instruments that have been specially designed for a given task must always be kept ready for use. Thus the inventory at present consists of 12 gas and 2 liquid chromatographs.

A gas chromatograph coupled to a mass spectrograph is also available to clarify the identity of any unknown substances. With the exception of this instrument, which has its own computer system, all the analytical instruments are controlled by a laboratory data system. The chromatographic data recorded are fed to a computer, which compiles a report from all the results. A copy of the printout is sent to the factory that commissioned the task; and another, to our Safety Department for statistical evaluation on a EDP storage medium.

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