USE OF DETECTOR TUBES IN ANALYTICAL CHEMISTRY

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ABSTRACT

The detector tube method is used frequently for measurements of gases. This is a colorimetric analysis technique, in which the gas sample is drawn through a glass tube filled with a reagent layer. A colour reaction takes place which is a measure of the gas concentration. Fields of application are workplace air analysis, technical gas analysis, testing of ambient air and usage in combination with laboratory methods.

INTRODUCTION

The detector tube method is a colorimetric analysis technique, in which a gas sample is drawn through a solid reagent layer by means of a pump. A reaction takes place resulting in a colour change of the preparation. The length or the intensity of the discoloration is a measure of the gas concentration. Detector tubes are, therefore, a laboratory method simplified to the extent that it can be employed as a rapid test in everyday practice.

Detector tube measuring systems are now highly developed. The main field of application is still workplace air analysis. The more notable recent advances have, however, been in the application of the detector tube method for technical gas analysis, for analysis of the ambient atmosphere and as part of laboratory methods.

Several independent national and international institutions have assessed the detector tube method and confirmed its reliability. Performance standards have been issued by these institutions, such as by the International Union of Pure and Applied Chemistry (IUPAC).

The purpose of this review is to show gas analysts both the advantages and limitations of the detector tube method. Detector tubes are easy to use, but this is no excuse for ill-considered application of the system. This review is, therefore, intended for the expert, who will critically examine whether detector tubes are the answer to the measuring task concerned before he uses them. The review should also give information how the detector tube method can be combined with complementary techniques, e.g., pyrolysis, to make it a versatile tool in analytical chemistry.

1. BRIEF RETROSPECTIVE VIEW OF INTRODUCING AND SIMPLIFYING GAS ANALYTICAL METHODS

The air in working areas can be contaminated by gases and vapours, but the concentration must not be at an arbitrarily high level. The health of those working in the area may be endangered when the concentration of the contaminants exceeds a critical level.

In this respect, an investigation of the ambient air with analytical equipment has to be carried out. The aim is to determine very small concentrations with the maximum reliability in a short time. Laboratory methods are not always suitable, since the time expenditure may be too high.

Hence, more than in any other analytical field, in air sampling it is desirable to have an apparatus with which reliable results of measurement can be obtained immediately on the spot.

Such a desire is a good reason to recall a few interesting data in the history of gas analysis.

The Dutchman van Helmont (1577 to 1644) was the first to make a clear distinction of the terms air and gas /1/. Although it had been observed earlier that there was a distinction between ordinary air and "air" obtained by distilling animal or vegetable matter or by the effect of acids on metals, no results are known which would permit the conclusion that these substances were regarded as gases.

For the first time after van Helmont, Joseph Black /2/ realized in 1755 that there are gases which have nothing to do with ordinary air. Black demonstrated that limestone contains "fixed air" which can be expelled by acids.

Cavendish then proved in 1766 that there are actually gases which differ from ordinary air. A few years later, several scientists (Lavoisier, Dalton, Cavendish, Gay-Lussac) employed various methods to determine that the oxygen content of air is about 21%. During his experiments, Cavendish even succeeded in detecting a gas which amounted to about the 1/120th part of air. It was not until over 100 years later that it was discovered that the residual gas observed by Cavendish were the noble gases.

Although additional publications of gas analytical investigations came out during the following decades, these methods were employed predominantly in the field of research. Bunsen presented the first teaching manual on gas analysis with his publication in 1857 /3/. Robert Wilhelm Bunsen is considered the founder of gas analysis; it is easy to understand that the gas analytical methods described by him yielded reliable results primarily in the laboratory and in the hands of skilled analysts.

A few decades passed before it was possible to design gas analysis in such a way as to meet practical requirements, i.e., to simplify a laboratory method to the extent that it could be employed as a rapid test outside laboratories. In the field of gas measurements such analyses became known commonly as detector tube analysis (Fig. 1). The first detector tube was developed in 1919 for determining CO /4/. The demand for such a device came from the U.S. mining industry; a measuring system was required which would reveal health risks directly at workplaces without great technical input. The inventors of the first detector tubes used a mixture of iodine pentoxide and disulfuric acid on pumice as carrier and called this preparation "Hoolamite". The Hoolamite was placed in thin glass tubes. If air containing CO was sucked through these tubes, the preparation changed colour to green. The CO content of the air sample could be estimated from the intensity of the discoloration (e.g., light green or dark green).

The number of new detector tubes is constantly increasing. The quality of such tubes has also reached such a level that the method has established itself in the field of gas analysis. The term "detector tube" covers a wide range of different versions; their common feature is an indicating layer enclosed in a transparent tube. Depending on reagent system, origin and usage conditions detector tubes provide qualitative indications or measurement results with an error of only a few percent.

The main field of application for detector tubes continues to be workplace air analysis. New areas are technical gas analysis and analysis of the ambient atmospheres. The potential uses of detector tubes have been considerably increased by the introduction of so-called long-term tubes for measurements lasting several hours. Detector tubes can thus be used for the following:

- Short-term analysis of workplace air (result obtained after some minutes).
- Long-term workplace measurement with special long-term detector tubes (determination of average concentration over several hours).
- Technical gas analysis with short-term tubes (process monitoring, emission measurements for technical installations).

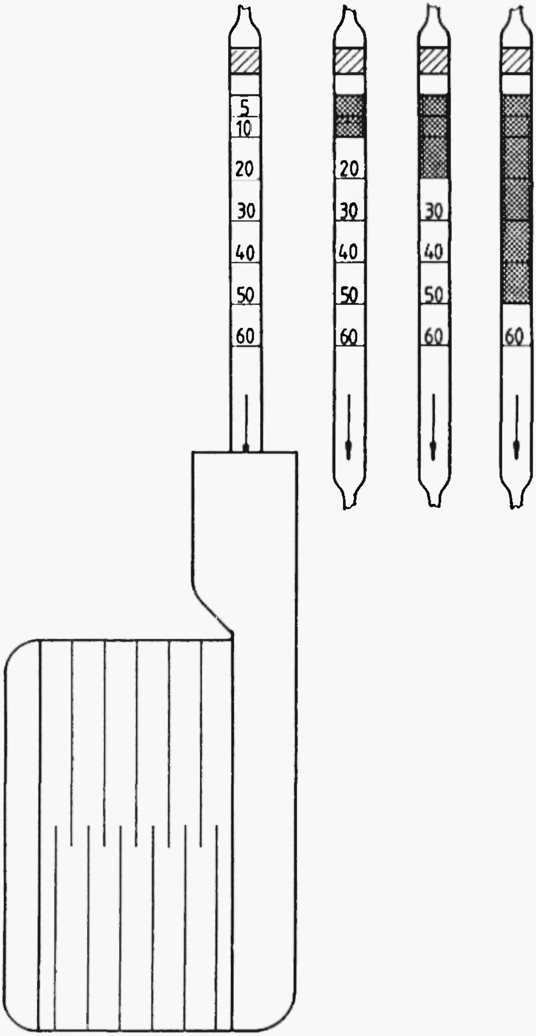


Fig. 1: Detector tube with hand-operated pump for the determination of gases. From left to right:

- Detector tube connected to the pump.
- After the test part of the indicating layer is discoloured (stain reaches scale mark "10")
- Test conducted at higher concentration (stain reaches scale mark "20")
- Test conducted at higher concentration (stain reaches scale mark "50")

- Long-term measurements in technical gas analysis using specially developed tubes (process monitoring, emission measurements for technical installations).
- Analysis of ambient atmosphere with short-term tubes featuring an extended measuring range (mean values, e.g., for 30 minutes).

This key-phrase list conceals a wealth of potential applications. Regular users of detector tubes are often surprised by the number of tasks in gas analysis which can be solved thereby.

2. CHEMICAL REACTIONS IN THE DETECTOR TUBE

A prerequisite for the use of reagents in detector tubes is a change in colour with the gas to be measured. This enables the amount of reagent used to be determined directly following the change of colour. The course of the reaction is thus made visible with detector tubes. Either the reagent changes colour directly, or the preparation additionally contains an indicator to show how much reagent has been used. Some of the numerous different reagent systems are outlined below:

a) Reaction of inorganic gas with inorganic reagent:

$$\mathrm{SO_2 + I_2 + 2\,H_2O \rightarrow H_2SO_4 + 2HI} \tag{1}$$

With this system there is a change in colour from brown to white; this method is used for detector tubes for performing measurements in the range between 20 and 70 000 ppm (v/v), i.e., in the higher-concentration range of SO_2.

Hydrogen sulfide exemplifies the variety of inorganic reagents suitable for such detector tubes:

$$\mathrm{H_2S + Pb^{2+} \rightarrow PbS + 2\,H^+} \tag{2}$$

$$\mathrm{3\,H_2S + 2\,Sb^{3+} \rightarrow Sb_2S_3 + 6\,H^+} \tag{3}$$

$$\mathrm{H_2S + Sn^{2+} \rightarrow SnS + 2\,H^+} \tag{4}$$

$$\mathrm{H_2S + 2\,Ag^+ \rightarrow Ag_2S + 2\,H^+} \tag{5}$$

$$\mathrm{H_2S + Hg^{2+} \rightarrow HgS + 2\,H^+} \tag{6}$$

$$\mathrm{H_2S + Cd^{2+} \rightarrow CdS + 2\,H^+} \tag{7}$$

$$\mathrm{H_2S + Ni^{2+} \rightarrow NiS + 2\,H^+} \tag{8}$$

$$\mathrm{H_2S + Co^{2+} \rightarrow CoS + 2\,H^+} \tag{9}$$

$$\mathrm{H_2S + Fe^{2+} \rightarrow FeS + 2\,H^+} \tag{10}$$

These reactions produce colour changes from white, green or pink to yellow, orange or black. Depending on the concentration range of the H_2S to be measured and the pH-value of the reagent systems further coloured metal compounds can be used.

b) Reaction of inorganic gas with inorganic reagent with the addition of an indicator:

$$SO_2 + I_2 + H_2O \xrightarrow{\text{starch}} H_2SO_4 + 2\ HI \qquad (11)$$

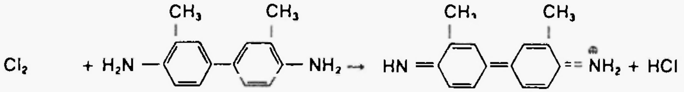
The addition of starch is chosen with this reagent system for tubes for measuring low SO_2 concentrations (measuring range 0.5 to 5 ppm). The colour of the iodine is not sufficient to indicate the amount of reagent consumed by way of a change in colour. On the other hand, the disappearance of the blue colour of the starch iodine complex is much more sensitive.

Examples for the reaction of further inorganic gases with inorganic reagents plus additional indicator:

$$2\ HCN + HgCl_2 \xrightarrow{\text{methylred}} Hg\,(CN)_2 + 2\ HCl \qquad (12)$$

$$CO_2 + H_2N\text{-}NH_2 \xrightarrow{\text{crystal violett}} H_2N\text{-}NH\text{-}CO\text{-}OH \qquad (13)$$

c) Reaction of inorganic gas with an organic reagent:



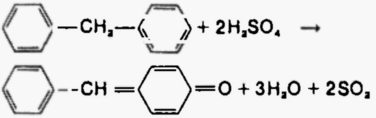
(14)

In this case the chlorine reacts with near colourless o-tolidine to form a yellow, quinoid compound.

Other aromatic amines are suitable instead of o-tolidine for the determination of chlorine. Several of these reagents, i.e., diphenyl benzidine, can also be used to measure nitrogen dioxide (NO_2 yields azo dye-stuffs with aromatic amines).

d) Reaction of organic gas with organic reagent:

(15)



The indicator preparation contains both formaldehyde and sulfuric acid as reagents. Condensation and the further reaction with sulfuric acid thus take place in one system. A reddish-brown quinoid compound is produced.

e) Reaction of organic gas with an inorganic reagent:

$$3\ C_2H_5OH + 4\ K_2CrO_4 + 10\ H_2SO_4 \rightarrow$$
$$3\ CH_3COOH + 2\ Cr_2(SO_4)_3 + 4\ K_2SO_4 + 13\ H_2O \qquad (16)$$

Ethanol is oxidized by chromate. The reagent system changes colour from yellow to green.

f) Transformation of the gas to be measured in a pre-layer and subsequent determination of the transformation product.

Reaction in the pre-layer:

$$CH_2 = CH - CN + Cr^{6+} \rightarrow HCN \qquad (17)$$

Reaction in the indicating layer:

$$2HCN + HgCl_2 \xrightarrow{\text{methyl red}} 2HCl + Hg(CN)_2 \qquad (18)$$

There is no known reagent system which produces a direct colour reaction with acrylonitrile in detector tubes. It is thus initially broken down in a pre-layer, with hydrogen cyanide being formed as a breakdown product. The subsequent reaction in the indicating layer with mercury chloride results in a change in colour from yellow to red in the presence of methyl red as an indicator.

Further examples for the transformation of gases to be measured in a pre-layer and subsequent determination of the transformation product:

Pre-layer: $C_6H_5Cl + Cr^{6+} + H_2SO_4 \longrightarrow HCl$
Indicator layer: HCl + bromophenol blue (19)

Pre-layer: $CHCl_3 + Cr^{6+} + H_2S_2O_7 \longrightarrow Cl_2$
Indicator layer: Cl_2 + o-tolidine (20)

Pre-layer: $HCON(CH_3)_2 + NaOH \longrightarrow (CH_3)_2NH$
dimethyl formamide (21)

Indicator layer: $(CH_3)_2NH$ + acid + bromophenol blue

Pre-layer: $CH_3Br + MnO_4^- + H_2SO_4 \longrightarrow Br_2$
Indicator layer: Br_2 + o-Dianisidine (22)

Pre-layer: $CHCl = CCl_2 + Cr^{6+} \longrightarrow Cl_2$
Indicator layer: Cl_2 + o-tolidine (23)

3. EVALUATION OF DETECTOR TUBE INDICATION

The length or intensity of the indication is evaluated depending on the course of the reaction.

Figure 2 shows a tube with a printed-on scale. The length of the colour change is evaluated on the printed scale after drawing in the prescribed volume of sample air. With the tube as per Figure 3, use is made of a colour matching for evaluation purposes. These tubes feature an integrated colour standard in addition to the indicating layer. The test procedure involves determination of the volume of sample air required to achieve colour matching between the reagent layer and colour standard. The concentration is then calculated from this volume.

The colour intensity of the indication is determined with tubes of the type shown in Figure 4. The volume of the sample air is specified; following completion of the test, the intensity is compared with a separate colour standard.

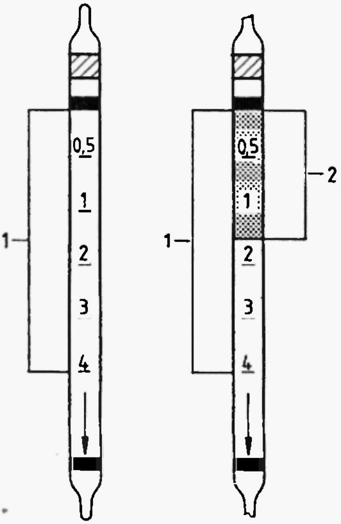


Fig. 2: Evaluating the indication on the printed-on scale 2.
1. Indicating layer (reagent layer)
2. Indicating (a numerical value of 1.5 results here)

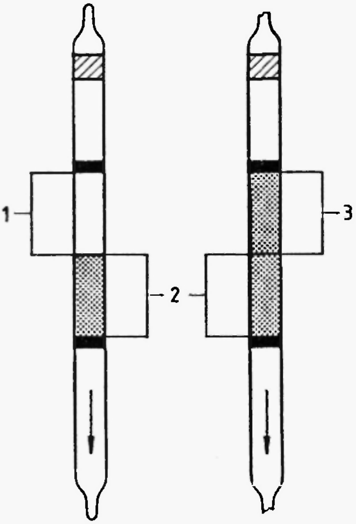


Fig. 3: Evaluating the indication by colour matching with an integrated colour standard
1. Indicating layer (reagent layer)
2. Colour standard
3. Reagent layer with indication (indication corresponds to colour standard)

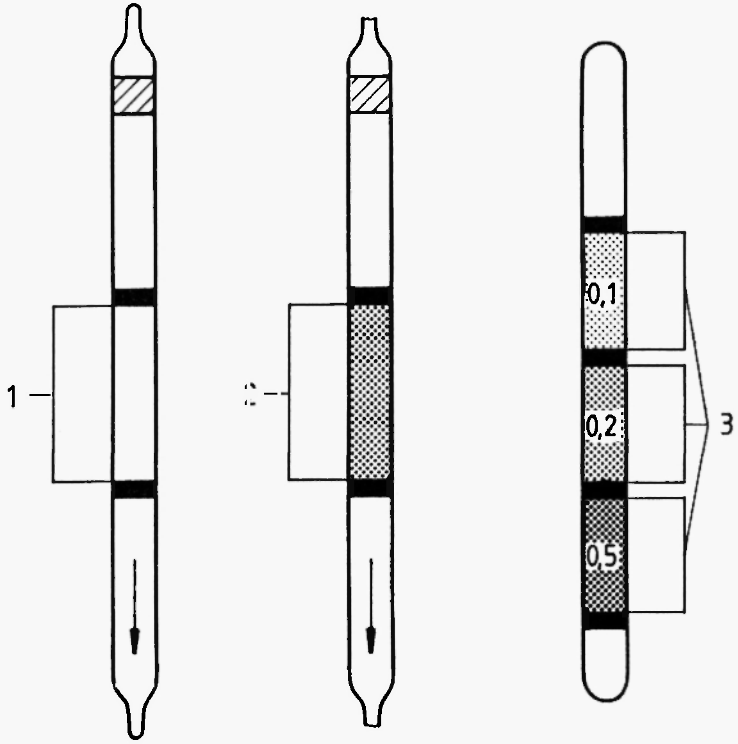


Fig. 4: Evaluating the indication by comparison with separate colour standards
1. Indicating layer (reagent layer)
2. Reagent layer showing indication
3. Colour standards (corresponding here to three different gas concentrations)

4. CROSS-SENSITIVITY OF DETECTOR TUBES

There are scarcely any reagents in chemistry which react specifically with a single component under all conditions feasible in practice. The cross-sensitivity of detector tubes with respect to interfering components is thus determined by the chemical properties of known reagent systems.

The cross-sensitivity of the reagents can often be reduced by filter layers in the detector tubes in which the interfering substances are absorbed while the component to be measured flows unimpeded through the filter layer and reacts as envisaged in the indicating layer.

Example: Detector tube for determining sulfur dioxide.

Suppose SO_2 is to be determined in the presence of H_2S. Use is made of sulfur dioxide l/a tubes. The tubes are filled with an indicating preparation and a pre-layer preparation containing a copper salt.

Without a filter layer, the hydrogen sulfide would react with the indicating layer:

$$H_2S + I_2 \rightarrow S + 2\,HI \tag{24}$$

However, H_2S reacts with the Cu compound in the filter layer while SO_2 does not.

$$H_2S + Cu^{2+} \rightarrow CuS + 2\,H^+ \tag{25}$$

The selectivity of unspecific reagents can, however, also be enhanced by using reagent mixtures. A combination of iodine pentoxide and fuming sulfuric acid reacts, for example, with numerous organic compounds (aliphatics, aromatics).

Different reactions of the indicating preparation with respect to aliphatics and aromatics (this reagent system is used in the detector tube for measuring gasoline) are obtained by selecting a definite sulfuric acid concentration and by adding a further oxidation agent (e.g. selenium dioxide). The aromatics are then measured with considerably less sensitivity, as they react with all three reagent components (I_2O_5, $H_2S_2O_7$, SeO_2). The aliphatics react only with I_2O_5. With equal concentrations of octane and toluene, the octane indication is roughly ten times larger than that of toluene.

A combination of oxidation agents and acids also permits other separations of various gases, as, for example, in two different types of detector tube for measuring hydrocarbons. One type of these tubes is intended for determination of liquified propane and butane. This tube contains iodine pentoxide and disulfuric acid as reagent. If we consider the alkanes, it becomes apparent that methane and ethane are not subject to any reaction whatsoever in the reagent system of this hydrocarbon detector tube. It is thus possible, for example, with this tube to substantiate C_3 and C_4 hydrocarbons in natural gas. Pentane and higher hydrocarbons are also indicated; however the indication sensitivity decreases with increasing molecular mass of the hydrocarbon.

The other type of hydrocarbon detector tube features selenium dioxide and disulfuric acid as reagent. The oxidizing properties of the reagent system are less pronounced than with the above-mentioned $I_2O_5 - H_2S_2O_7$ mixture. A reaction and thus a colour indication take place only with hydrocarbons from pentane onwards.

5. PUMPING DEVICES FOR DETECTOR TUBES

The rate at which the gas flows through the detector-tube reagent system has a considerable effect on the indication. Excessive speeds result in an incomplete reaction. If the flow rate is too low, secondary reactions may take place. In both cases the indication differs from the desired value. Positive errors accompany an excessive volumetric flow rate, negative errors are encountered with secondary reactions. The reagent properties of the detector tubes must therefore be matched to the suction behaviour of the pump. This leads to an important prerequisite in practice, namely that pumps and tubes are a unit. This means that pumps and tubes produced by different manufacturers may not be interchangeable.

In most cases, the so-called bellows pumps are used in conjunction with detector tubes. They are hand-operated and draw in 100 cm^3 per stroke, depending on the type of tube (flow resistance of filling preparation). The duration of a pump stroke is between roughly 3 s and 60 s. The bellows pump can also be operated automatically via an electric motor.

Bellows pumps are used in conjunction with the so-called short-term tubes. The hand operated bellows pump is preferred for single measurements and a few strokes (e.g. up to 30 strokes); the automatic bellows pump is employed for frequently repeated individual measurements (strokes as for hand operated pump). It is, however, primarily utilized for measurements with more strokes (i.e. extending the measuring range of the detector tubes by increasing the number of strokes).

6. QUALITY OF DETECTOR TUBES

6.1 Performance Standards for Detector Tubes

One can expect that all major detector tube manufacturers have established a quality assurance system to maintain a high-quality standard of their products. In most cases these manufacturers follow performance standards issued by official and international organizations. The International Union of Pure and Applied Chemistry (IUPAC), for example, has published a performance standard for detector-tube units /5/ and also proposals for generating test gases for calibration of detector tubes /6/.

In the IUPAC detector-tube standard the following requirements are laid down:

- Properties of the aspirating pump.
- Information to be supplied by the manufacturer on the reactions involved in the detector tubes and the levels at which other gases and vapours are likely to interfere.
- Properties of the detector tubes (temperature range in which detector tubes can be used; shelf life, etcs.).
- Measuring range.
- Indicating error.

Depending on the class of detector tubes and the concentration range the indicating error shall not exceed 25% (class A) or 50% (class B); the measuring results should be within these specification limits with a confidence of 95%.

6.2 Brief Explanation of the Manufacture and Calibration of Detector Tubes

A production batch of detector tubes usually numbers approximately 10,000. These tubes have to be manufactured with the utmost care and uniformity. A reproducible indication response of the detector tubes within a production batch must be achieved thereby. Within a batch of carefully manufactured detector tubes the indicating properties fluctuate less than 5% (repeatability of measuring results). Such a high standard is achieved by a comprehensive quality assurance which starts with the manufacture of the filling preparations and includes all phases of production and calibration of the detector tubes. Random samples for tests and calibration with defined gas concentrations are taken in accordance with statistical rules, i.e. at least 150 detector tubes are taken from each production batch (of 10,000 tubes) and tested. That requires the manufacturer to compile at least 150 results which can be used to establish the calibration curve of the batch of detector tubes.

6.3 To Which Extent does the User Rely on the Detector-tube Quality, Specified by the Manufacturer

The user of detector tubes has various possibilities for accepting this measuring system for his analysis.

First:

The user relies on the data provided by the manufacturer in operating instructions, detector-tube handbooks, and other brochures. This is probably the most frequently practised procedure. If the detector-tube manufacturer maintains a recognized and approved system of quality assurance, the user can be reasonably confident that he has a reliable measuring system at his disposal.

Second:

The user ascertains by visits to the manufactuer's plant under which conditions the detector tubes are manufactured and calibrated. The manufacturer of the detector tubes will not make any secret of the production steps and laboratory methods which determine the quality. A visitor should therefore obtain information from the manufacturer giving the possibility to make reliable evaluation of the detector-tube quality.

Third:

The user of the detector tubes can recalibrate the detector tubes in his laboratory by checking a representative sample of the detector-tube shipment by means of test gases (such as two or three detector tubes per package of ten). It should be emphasized specifically at this point that a very well equipped laboratory is needed for the generation of defined test-gas concentration. A competent gas analyst is also needed who has the necessary practical experience in this special field. If the user has recalibrated a representative portion of the detector tubes, it can be expected with a high degree of statistical confidence that the remaining detector tubes from the same batch have the same properties. But in view of the high technical input, recalibration of detector tubes by the user will be limited to a few exceptions.

7. DETECTOR TUBES FOR SPECIAL ANALYSES

Measurements with detector tubes are standard practice. In addition to workplace air analyses, detector tubes are now also used for analysing the ambient atmosphere and for monitoring emissions. Of particular interest to the analyst is, however, the use of detector tubes as part of laboratory methods.

The reactions taking place in detector tubes are known; the user can thus assess the range of application.

In the following paragraphs some examples are given for using detector tubes in the framework of special analysis.

7.1 Method of Rapidly Determining Solvent Residues in Extracted Oils

Many of the vegetable oils used in food are obtained by extraction. For this purpose, milled or pre-pressed oil seeds as well as oil-containing by-products are treated with solvents (e.g. naphtha, hexane, trichloroethylene).

Small residual quantities of the solvent used for extraction can never be completely avoided in the unrefined oil.

In practice, we are faced with the task of determining this residual-solvent content in the shortest possible time.

The following methods are known at present:

a) Determination of dry residue (in drying oven) and additional moisture determination; the amount of solvent is then calculated from the difference between total volatiles and water.
b) Expulsion of solvent at 180° in a stream of nitrogen and subsequent adsorption on activated charcoal.
c) Gas chromatography.

Pardun et al. /7/ came to the conclusion that all these methods are too time-consuming or too sophisticated in terms of apparatus. They can thus not be performed by untrained personnel. It is therefore suggested that the detector-tube method be employed.

The following specification applies to the determination of extraction naphtha: A defined amount of the extracted oil to be tested is poured into a washing bottle. The solvent residues are expelled with a jet of air (flow rate 3 litres per hour for 10 minutes). A diaphragm pump is used to convey the air. Following absorption of volatile oxidation products of the oil on potassium hydroxide (U-tube) the naphtha-containing air is routed through the hydrocarbon detector tube, where the naphtha reacts with the reagent (selenium dioxide and disulfuric acid) and turns the yellow indicator layer brown. The length of the colour change is evaluated. The detection limit is 0.01% naphtha.

The apparatus is calibrated with test oils produced from solvent-free oils and corresponding quantities of hexane. There is a linear relationship between the length of the colour change in the detector tube and the naphtha concentration of the oil.

Trichloroethylene determination in extraction oils can also be effected in a similar manner. For this purpose use is made of trichloroethylene tubes. Here, too, a special calibration curve is employed, which has to be determined with test oils of known composition.

7.2 Determination of Organically Bonded Sulfur in Coke-Oven Gas

The service life of gas appliances is influenced amongst other things by the organic sulfur compounds in pipeline gas. To date, the natural gases used have been largely free from sulfur. Exploration results have, however, shown that more and more sulfur-containing natural gas is to be expected in future.

It thus became necessary to establish the maximum permissible organic-sulfur content. At the same time, however, an analytical method had to be found which was capable of determining organically bonded sulfur in the range of approximately 100 mg S xm^{-3}.

For the determination of such small concentrations, standard analytical methods require large samples, in some cases more than 100 litres of gas. Plankert /8/ thus recommends H_2S detector tubes for the determination of organically bonded sulfur. He considers the detector-tube method to be sufficiently reliable particularly for the requirements of coking plants. The major advantage is the short analysis time coupled with the small sample volume.

The hydrogen sulfide is initially removed from the gas to be analysed in a cadmium acetate solution. The organic sulfur compounds are then reduced at roughly 1000°C to H_2S at a platinum contact.

To assess the proposed analytical method, Plankert investigated test gases with a specified organically bonded sulfur content (use was made of thiophene); in the least favourable case the deviation from the desired value was 6% (relative). Six coking plants took reference measurements in order to test the method. At the same time, coke-oven gas was analysed in accordance with the reference laboratory method (oxidation to sulfate); the maximum deviation between detector tubes and reference method was 4.8% (relative).

7.3 Determination of Small Quantities of Sulfur in Liquid Hydrocarbons with the Aid of Hydrogen Sulfide Detector Tubes

The lowest possible sulfur content of the starting products is required for catalytic conversion of hydrocarbons. The maximum permissible sulfur concentrations are a function of the catalyst employed, but generally speaking, they should be less than 20 ppm. Some compressive breakdown methods for producing rich gas require less than 0.2 ppm.

Mackinger /9/ has stated that there are various analytical methods of quantitatively determining the total sulfur in liquid hydrocarbons. These methods can however only be implemented in well-equipped laboratories on account of their sophistication.

Generally speaking, the Granatelli method, where the organic sulfur compounds are reduced by Raney nickel, can be put to good use. The hydrogen sulfide liberated upon acidification (with HCl) has been determined photometrically using the methylene-blue method or by way of titration with mercury acetate. The measurement results are however subject to considerable scatter in the case of sulfur contents of less than 10 ppm and with samples with contain olefin.

The scatter can be considerably restricted by using the Granatelli method for reducing the sulfur compounds (in special apparatus) to nickel sulfide with Raney nickel. Once this reaction has been completed, the outlet of the reflux condenser is connected to a hydrogen sulfide detector tube. The passage of gas through the detector tube should be from top to bottom, so as to prevent backwash.

Nitrogen (free of oxygen) is routed at a rate of 5 to 10 $L \times h^{-1}$ through the apparatus and through the detector tube. Acidification is then effected with a mixture of hydrochloric acid and propanol. This is followed by heating. Evaluation takes place once the length of the colour change in the H_2S detector tube has stabilized. The blank reading is also determined.

The results of sulfur determinations using detector tubes differed less than 5% (relative) from the theoretical value.

7.4 Method of Rapidly Determining Arsenic in Soils and Related Materials and in Water

Arsenic is an important indicator in geochemical prospecting for ore deposits. It was thus necessary to develop a rapid method of determining the arsenic content of soil and water samples under field conditions.

Krings et al. /10/ developed simple analytical apparatus consisting of an Erlenmeyer flask, a small rubber balloon, a detector tube for determining the arsine and a bellows pump. The arsenical sample was treated with zinc and diluted sulfuric acid. The arsine produced during the reaction was routed through the detector tube. The results of As determination using laboratory methods and detector tubes showed good agreement. Concentrations down to 10mg As per kg sample could be measured.

7.5 Determination of Sulfides in Water-Based Drilling Fluids

When drilling for oil and natural gas, a prerequisite is rapid analysis of the drilling fluid with respect to sulfides. The American Petroleum Institute recommends the use of detector tubes in conjunction with the so-called Garrett Gas Train /11/. The "Gas Train" essentially consists of three gas washing bottles, a small CO_2 compressed-gas cartridge, a pressure reducer and a flowmeter combined in a plastic block.

Method: The sample is fed into the apparatus, H_2S is liberated by sulfuric acid and flushed through the H_2S tube with carbon dioxide. The tube reading is a direct indication of the hydrogen sulfide content of the drilling sample.

7.6 Measurements of Chemical Contaminants in Soil Water Samples by Means of Detector Tubes

In order to measure pollutants in the soil or in water by detector tubes Mussmann /12/ proposes a simple method. The relevant sample was introduced in a small vessel (e.g. 250 cm^3 gas scrubbing bottle with frit inset). About 50 g of material should be inserted in the case of soil samples, and about 100 cm^3 in the case of liquid samples. The appropriate detector tube (selected according to the substance to be detected) is inserted into the gas detector pump and connected to the scrubbing bottle by a short hose (glass-to-glass). The gas detector pump is then actuated, air is thus drawn through the soil or liquid sample and, therefore, through the tube as well. In many cases the chemical pollutant will volatilize as a result of this aspiration process. If a sufficient concentration is present in the gaseous phase, the filling in the detector tube changes its colour.

If chemicals, such as acids, are added, compounds can be released that would otherwise yield concentrations difficult to measure because of their low volatility. Example: sulfuric acid to detect cyanide in soil samples.

Table 1 lists a selection of substances which can be detected in soil samples with detector tubes. The concentration of the pollutants measured under laboratory conditions is listed in mg per kg for a colour change of the indicating layer up to the first graduation mark of the tube scale or, in the case of colour comparison tubes, to the first distinct colour change.

TABLE 1: POLLUTED SOIL SAMPLES

Pollutant	(Lowest measurable concentration, approx.) mg/kg
acetone	50
benzene	50
chlorobenzene	10
diethyl ether	50
dichloromethane	200
tetrachloroethene	20
toluene	50
trichloroethene	20

Table 2 lists a selection of substances which can be detected in water samples with detector tubes. The concentration of the pollutants measured under laboratory conditions is listed in mg per litre for a colour change of the indicating layer up to the first graduation mark of the tube scale or, in the case of colour comparison tubes, to the first distinct colour change.

The concentrations listed in Tables 1 and 2 have been measured in laboratory tests. All measurements were carried out at approximately 20°C. The detected substances were added to the samples in pure form. If several pollutants are present at the same time in a soil or water sample, other detection limits may possibly result. It should be considered that reactions (e.g. hydrolysis) may occur in the case of some chemical pollutants in soil or water samples depending, e.g. on the influence of the temperature and time. Such converted substances can generally not be detected by means of detector tubes. The detection limits listed in the tables should, therefore, be considered only as orientation data for qualitative detection.

TABLE 2: Polluted Water Samples

Pollutant	(Lowest measurable concentration, approx.) mg/l
acetaldehyde	10
acetone	1
acrylonitrile	2
alcohol (ethanol)	500
ammonia (aqueous solut.)	0.5
benzene	1
carbon disulfide	0.5
chlorobenzene	1
1-chloro-2,3-epoxypropane	0.1
2-chloro-1,3-butadiene	0.1
cyclohexane	5
diethyl ether	1
dimethyl sulfide	1
ethyl acetate	50
ethyl benzene	1
mercaptan	0.2
dichloromethane	1
n-hexane	10
n-pentane	10
n-octane	5
tetrachloroethene	0.1
tetrachloromethane	0.1
toluene	0.5
1,1,1-trichloroethane	3
trichloroethene	0.1
triethylamine	30

7.7 Combination of Detector Tube Measuring Methods and Pyrolysis Devices

7.7.1 General: Not all the substances occurring as air pollutants can be measured by means of detector tubes, including gaseous compounds which have a particularly high degree of chemical stability. High chemical stability generally infers low reactivity with consequential non-response of the detector tube reagent systems. At least in some cases, however, it appears to be possible by thermal conversion (pyrolysis) to obtain from inert substances products which can then be measured by means of detector tubes.

Pyrolysis is a well-known procedure in chemical analysis. Carefully controlled pyrolysis conditions lead to products of oxidation or decomposition, whose concentration is related to the concentration of the starting products.

The combination of detector tube measuring methods and a pyrolysis device is illustrated below by some examples:

7.7.2 Experimental conditions: The following substances were used for the experiments:

Halothane ($CF_3CHClBr$)
Methane (CH_4)
Halon 1211 (CF_2ClBr)
Refrigerant R 113 (CF_3CCl_3)
Chloromethane (CH_3Cl)
Sulfonyl fluoride (SO_2F_2)

The test equipment is shown schematically in Figure 5. A

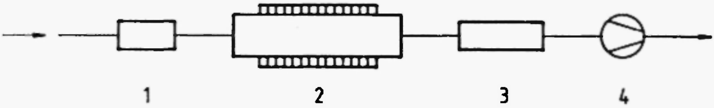


Fig. 5: Pyrolysis system upstream of detector tube for measuring substances of high chemical stability

1. Pre-tube (drying agent)
2. Tubular oven (temperature-controlled) with quartz tube
3. Detector tube
4. Pump

commercial tube furnace with temperature control was used for pyrolysis (dimensions of the quartz tube inserted into the furnace; outside diameter 7 mm, inside diameter 5 mm, length of the heated tube section 180 mm). The detector tubes and the corresponding suction pumps were also commercial models. The concentration of the substances to be measured was set in air according to the IUPAC proposals /6/.

In order to avoid hydrolysis effects of the decomposition products, the test air was dried with magnesium perchlorate in the halothane, halon, refrigerant and chloromethane experiments, before it entered the tube furnace. Pyrolysis of methane and sulfonyl fluoride was carried out in moist air (approximately 10 mg H_2O dm^{-3}).

The pyrolysis products which were characteristic for the substance were determined in each case by short-term detector tubes.

7.7.3 Results:

a) Halothane ($CF_3CHClBr$)

As per Table 3, a temperature of 900°C was chosen as operating temperature for the pyrolysis. (The test air was dried before it entered the pyrolysis furnace.)

TABLE 3: Halothane ($CF_3CHClBr$); Results of Halogen Splitting ($Cl_2 + Br_2$)

Volume concentration Halothane ppm	Temperature °C	Indication of the chlorine short-term tubes (the tubes measure the sum $Cl_2 + Br_2$) ppm
5	600	0.5
5	700	2.5
5	800	3.2
5	900	3.5
5	1000	3.5

The results of the measurements carried out by means of short-term detector tubes are compiled in Figure 6. Ten measurements each were carried out at the volume concentrations listed (1; 2.5; 5; 7.5; 10 ppm halothane); the coefficient of variation of the results was about 15%.

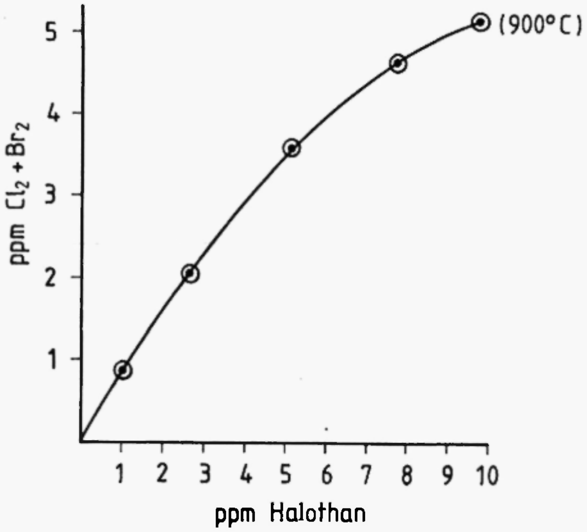


Fig. 6: Results of halothane ($CF_3CHClBr$) measurements using a pyrolysis system combined with detector tubes. Halogen concentration ($Cl_2 + Br_2$) as a function of the halothane concentration.

b) Methane

Table 4 shows that a temperature of at least 800°C is needed to trigger the oxidation of CH_4 to CO. At temperatures over 950°C, the CO yield dropped due to CO_2 formation.

TABLE 4: Methane (CH_4); Results of CO Formation

Volume concentration Methane ppm	Temperature °C	Indication of the CO short-term tubes ppm
100	700	1
100	800	15
100	850	20
100	900	25
100	950	40
100	1000	20

Temperatures of 900°C and 950°C were chosen as operating temperature (humidity of the test air about 10 mg H_2O dm^{-3}).

The CO concentrations were determined by means of the appropriate short-term CO detector (dual measurements in each case). Some CO_2 determinations were carried out additionally.

The results shown in Figure 7 indicate that there is a definite correlation between the CO formation and the methane concentration in the range from 50 to 1000 ppm of CH_4, both at 900°C and at 950°C.

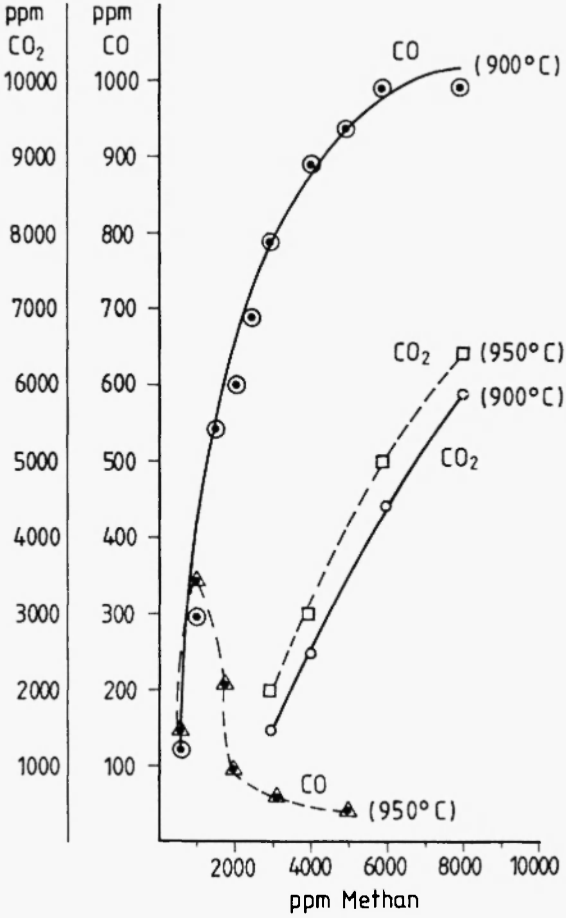


Fig. 7: Results of CH_4 measurements using a pyrolysis system in combination with detector tubes. CO and CO_2 concentration as a function of temperature and CH_4 concentration

Difference in the CO yields for these temperatures, however, yielded CH_4 concentrations over 1000 ppm.

In the system heated to 900°C, the CO concentration increased with increasing CH_4 concentration (as was desired, incomplete combustion took place). At 950°C the CO yield dropped suddenly but this was accompanied by parallel CO_2 formation. (Combustion of the CH_4 leads to a rise in temperature in the system; high CH_4 concentrations locally raise the temperature to a range in which – simply put – complete combustion to CO_2 dominates so that a lower CO yield is to be expected.)

c) Halon 1211 (CF_2ClBr)
Refrigerant R 113 (CF_3CCl_3)
Chloromethane (CH_3Cl)
Sulfonyl fluoride (SO_2F_2)

In all tests, only one of the substances mentioned was present in the test air. The results (dual measurements by means of short-term tubes) and the test conditions have been compiled in Tables 5-8.

Halon furnished chlorine and bromine as decomposition products. The sum of these substances was measured. Decomposition of the refrigerant R 113 led to formation of chlorine (subsequent chlorine measurement). The same holds for chloromethane. Sulfonyl fluoride decomposed while SO_2 was formed which was measured.

TABLE 5: Halon 1211 (CF_2ClBr); Results of Halogen Splitting ($Cl_2 + Br_2$)

Volume concentration Halon 1211 ppm	Temperature °C	Indication of the chlorine short-term tubes (the tubes measure the sum $Cl_2 + Br_2$) ppm
100	800	75
100	850	90
100	900	70
100	1000	60
100	850	90
500	850	250
1000	850	400

TABLE 6: Refrigerant R 113 (CF_3CCl_3); Results of Cl_2 Splitting

Volume concentration R 113 ppm	Temperature °C	Indication of the chlorine short-term tubes ppm
100	850	4
100	1000	5
25	850	0.5
100	850	4
200	850	8

TABLE 7: Methyl Chloride (CH_3Cl); Results of Cl_2 Splitting

Volume concentration ppm	Temperature °C	Indication of the Cl_2 short-term tubes ppm
50	800	0.1
50	900	0.2
50	950	0.4
50	1000	1.5
50	1100	0.9
50	1200	0.6
5	1000	0.2
10	1000	0.3
50	1000	1.5
100	1000	3

TABLE 8: Sulfonyl Fluoride (SO_2F_2); Results of SO_2 Splitting

Volume concentration SO_2F_2 ppm	Temperature °C	Indication of the SO_2 short-term tube ppm
10	900	1
10	1000	3
10	1100	4
10	1200	5
10	1300	6
5	1200	3
10	1200	5
50	1200	13
100	1200	22

8. EXPLANATION OF THE CALIBRATION CURVES OF DETECTOR TUBES

8.1 General

The indication obtained with detector tubes is a measure of the gas concentration. For scale tubes, the relationship between indication (length of the discolouration) and gas concentration can be described by curves like these shown in Figure 8. On evaluation of such calibration curves, it can be seen that there is a linear relationship between indication and concentration for only a few detector tube types. In the majority of cases, a curved line is observed. As will be shown, however, "curved" calibration lines also follow given mathematical relationships.

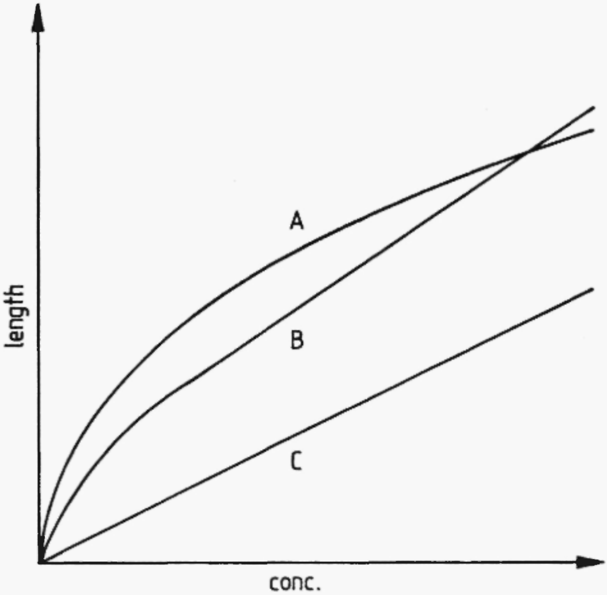


Fig. 8: Calibration curves of detector tubes (length of indication versus gas concentration).
Curve A) curved throughout its length
Curve B) curved initially and then linear
Curve C) linear throughout.

For practical reasons, the indication of the detector tube is usually given in units of the measured quantity (e.g. 50 ppm). Many tubes, however, have also been calibrated in absolute quantitites (e.g. μg, μl); i.e., in these tubes, the product of sample volume and gas concentration is constant.

Example:

CO detector tube

Concentration by volume: (c) in ppm CO	500	100	10
Air sample volume (V) in litres	0.2	1	10
Length of indication in mm	30	30	30
Product c x V	100	100	100

8.2 Relationship between Length of Indication and Mass of Gas

According to Leichnitz the following relationship can be drawn between the length of the indication and the mass of gas /13/:

$$\boxed{l = \frac{m}{C} + \frac{v}{A}\left(1 - e^{-l\frac{A}{v}}\right)}$$

l = length of the indication (mm)
v = flow rate of the gas sample in the tube
A = a constant (measure of the rate at which the gas component to be determined reacts with one layer element)
e = 2.718
m = the total mass of the gas component absorbed (μg)
C = the absorption capacity of one layer element with respect to the gas component

8.3 Deviation of the Calibration Curve from Equation

The equation according to chapter 8.2 is not valid for all detector tube calibration curves. Even on the basis of theoretical considerations, tubes can be picked out in which the calibration curve cannot correspond to this equation.

Firstly: The absorption capacity C of a layer element is not constant, but depends on the gas concentration c of the gas component to be determined. This dependence is always present when the reaction of the gas component with the reagent is not quantitative, but takes place with the formation of an equilibrium. The equilibrium position of this reaction is a function of the gas concentration c; i.e. the absorption capacity C increases with increasing gas concentration. The length of the indication then depends, not only on the mass of the gas component to be determined, but also on its concentration c.

Detector tubes of this type cannot be calibrated in absolute quantities, since the product of gas sample volume and gas concentration is not constant.

Secondly: The mass of gas m reacting with one layer element may not be constant, since part of the gas component is adsorbed by the carrier material. Under these conditions, two separate sorption processes take place in a layer element, one being a chemical reaction with the reagent and the other physical adsorption by the large surface of the carrier material. The mass of gas m_A adsorbed on the carrier material is a function of the gas concentration. Thereby, however the mass of gas m_R available for reaction with the reagent also becomes a function of the gas concentration c:

$$m_R = m - m_A$$

The mass of gas m_A adsorbed per layer element can be calculated from the Freundlich adsorption isotherm:

$$m_A = a \times c^b$$

a and b are constants, c is the gas concentration.

From the equation according to paragraph 8.2, we then obtain:

$$\boxed{l = \frac{m - a \cdot c^b}{C} + \frac{v}{A}\left(1 - e^{-l\frac{A}{v}}\right)}$$

Since the mass of gas adsorbed (a x b^b) becomes smaller with decreasing concentration for this type of detector tube, a gas concentration results, below which the equation according to chapter 8.2 is again valid, i.e. the length of the discoloured zone then depends only on the mass of gas to be determined and not on the gas concentration. With tubes of this type, lower gas concentrations can be determined more reliably than high concentrations.

Calibration curves of detector tubes, which, for practical reasons, are used for the determination of higher gas concentrations, i.e. concentrations in which the adsorption effect is strongly apparent, can be brought to correspond to equation 8.2 by the following procedure. After sucking in the gas sample to be investigated, clean air is sucked through the tube to desorb the adsorbed gas and bring it into reaction.

Thirdly: If the reagent system of the detector tube consists of several components, it is possible for the gas to react with more than one reagent component: e.g. Alcohol detector tube with reagent system potassium dichromate + sulfuric acid. In this case, the alcohol vapour to be determined is not only oxidised by the chromium (VI) compound, but also reacts with the sulfuric acid, forming an ester. The concentration of the ester formed, however, depends on the concentration of the alcohol vapour, so that the total absorption capacity C depends on the gas concentration c. A somewhat more reliable reaction course in the Alcohol detector tube is obtained only because the esterification is slower than the oxidation. It is possible to exclude esterification almost completely by increasing the flow rate of the gas sample in the tube, whereby the oxidation reaction dominates. For practical reasons, however, it is not possible for the flow rate to be arbitrarily increased, so that esterification persists as an undesirable side reaction. Even from these general considerations, it can be seen that the indication in tubes of this type can be strongly dependent on the rate of flow. The side reaction is particularly noticeable with low flow rates and leads to a considerable shortening of the discoloured zone.

Fourthly: Finally, we must consider those reactions in which transfer from the gaseous phase to the indicating preparation is so slow that a delimitation of the discoloured zone can barely be detected (colour comparison tubes). Here the entire indicating layer changes colour even after sucking through small gas volumes. The intensity of the colour indication then increases with increasing volume, again over the entire indicating layer. Evaluation of the indication of such detector tubes takes place by comparison with a colour standard.

9. CONCLUSIONS

It becomes clear from this brief review that detector tubes are a useful tool in the field of gas analysis. New guidelines and regulations require additional analyses of gases. In this connection the question must be raised as to whether the existing analytical potential is sufficient to cope with the measuring tasks involved. At this point it would be appropriate to include the detector tube method regularly into gas analysis. The detector tube method has the advantage of clarity as regards its potential application. With detector tubes, for example, it is possible to make an immediate statement about the indication behaviour in advance. Detector tubes represents a 'prepared analysis'; they can be described as a type of 'analytical reserve'. If detector tubes are manufactured within the framework of an approved quality assurance system, then the properties of the tube will be within the specified tolerances in each case. This means it is possible to stipulate the range and the limits of application for each type of tube in advance with a high confidence level.

It is important that the detector tube should not only be regarded as an end in itself, but to note that it can be combined with other gas analytical methods. Thus even suitable to test liquids and solid substances, especially in this field the detector tube method deserves more attention than it often receives.

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