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ANALYSIS OF TRACE IMPURITIES BY GAS CHROMATOGRAPHY

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CONTENTS

1. Introduction 330

2. Features of chromatographic trace impurity analysis 331
   - Separation criteria 331
   - Sample size 331
   - Impurity accumulation 332
   - Quantitative interpretation of the chromatograms 333

3. Trace impurity analysis with large samples 333
   - Isothermal separation of large samples 333
   - Elimination of the main constituent 334
   - Enrichment as a result of thermal effects on the column 336

4. Trace impurity analysis with high-sensitivity detectors 336

5. Determination of trace impurities in complex mixtures 336

1. INTRODUCTION

The extensive and varied advances made in gas chromatography range from analytical studies on mixtures of several constituents on the one hand to trace analysis of minor constituents in various systems on the other hand. The latter type of problem is of great importance in the polymer industry, where high-purity monomers are often required. In some cases, even very small traces of certain impurities in the monomer can alter the course of the polymerisation reaction and mar the final product.

Whereas high precision is the foremost requirement in the analysis of complex mixtures, trace analysis relies primarily on high-sensitivity methods. Present-day gas chromatography techniques in their conventional, unmodified form can detect components present at a level of a few hundredths of one per cent. We shall therefore apply the term "trace constituent" to substances whose concentration in the sample is of the order of 0.001% or less.

Chromatographic methods of trace analysis are reviewed in the present article. The chromatographic analysis of complex organic systems has been previously discussed[1] by one of us.

2. FEATURES OF CHROMATOGRAPHIC TRACE IMPURITY ANALYSIS

Separation Criteria

The criterion most commonly employed to characterise the degree of separation (*i.e.* the resolution) of chromatographic peaks is the quantity

$$K = \frac{l_{(2)} - l_{(1)}}{\mu_{(1)} + \mu_{(2)}}, \quad (1)$$

where $l_{(1)} - l_{(2)}$ is the difference between the ordinates of the peaks on the chromatogram, and μ is the peak width, measured[2] at some chosen fraction of the maximum peak height, h. Thus, the half-width $\mu_{0.5}$, is measured at a height of 0.5 h, the width μ_e at a height of $(1/e)h$.

This criterion has been shown[3] to be satisfactory only when the peaks are well resolved, and when the substances are present at comparable concentrations ($\varphi \simeq 1$, where φ is the ratio of the corresponding peak heights). When the constituents are present in widely different concentrations, it has been suggested that the width of the larger peak should be measured at the same height as that of the smaller peak:

$$K = \frac{l_{(2)} - l_{(1)}}{\mu_{(1)} \sqrt{\ln\varphi + 1} + \mu_{(2)}}, \quad (2)$$

where the subscripts (1) and (2) refer to the main and the trace constituent respectively. Thus modified, the formula represents the degree of separation far more realistically, since Eqn. (1) can give $K = 1$ (for very large φ) even at very modest peak resolutions.

It can be shown that complete separation ($K = 1$) of two nearly equal peaks requires a minimum length of column given by the expression

$$L = 44.36 \frac{\left(\frac{\varkappa}{\varkappa_1} + \Gamma\right)^2}{\Delta\Gamma^2} \frac{D\varkappa}{\alpha}, \quad (3)$$

where $\Delta\Gamma$ is the difference between the Henry coefficients of the first (Γ_1) and the second (Γ_2) constituent, Γ the mean of the two coefficients, $\varkappa$ the fractional free volume of the column, $\varkappa_1$ the fractional volume occupied by the liquid phase, α the linear velocity of the carrier gas, D the effective coefficient of longitudinal diffusion, and the numerical factor 44.36 indicates that peak half-widths are used in the calculation.

In trace analysis, complete separation of the peaks requires a length of column

$$L = 11.09 \left[\frac{\left(\frac{\varkappa}{\varkappa_1} + \Gamma_2\right) + \left(\frac{\varkappa}{\varkappa_1} + \Gamma_1\right)\sqrt{1 + \ln\varphi}}{\Delta\Gamma}\right]^2 \frac{D\varkappa}{\alpha}. \quad (4)$$

It follows that longer columns, or more selective adsorbents, are needed to improve the separation of trace impurities.

In many cases complete separation cannot be achieved, and neither $\mu_{(2)_{0.5}}$ nor $\mu_{(2)_e}$ are measurable. Some subsidiary criteria have been proposed to characterise the resolution of overlapping peaks: the quantity θ, for example, is defined[4] as

$$\theta = \frac{f}{g} \times 100, \quad (5)$$

where f and g are the distances indicated in Fig. 1: f is the distance, measured normal to the base-line, between

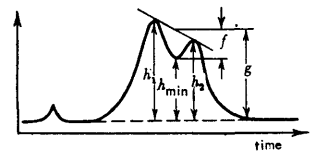


Fig. 1. Parameters of incompletely resolved chromatographic peaks.

the minimum and the tangent to the two maxima, $g = f + h_{\min}$.

In trace analysis, however, the maximum of the main peak is often inaccessible, and the extent of resolution cannot be calculated in this way. One must then turn to the criterion

$$\psi = \frac{h_2 - h_{\min}}{h_2}, \quad (6)$$

which defines the degree of resolution in systems where the main peak is very much larger than the impurity peak, and cannot be plotted on the chromatogram even if full use is made of the sensitivity control (Fig. 2).

However, since fairly large samples are used in the separation of trace impurities, the separation criterion is a function of sample size as well as of experimental conditions. With variable sample sizes, therefore, the most rational criterion is obtained by multiplying ψ by some function of the sample volume.

Sample Size

Samples used in gas chromatography are mostly between 0.5 μl and 0.1 ml (liquids) or 0.1 ml and 20 ml (gases). The use of still larger samples results in wider (as well as higher) peaks, so that neighbouring peaks tend to overlap. Van Deemter *et al.*[5] determined the permissible sample volume v_p for which the peak width is independent of the volume of material under test, and showed that v_p is equal to one-half the product of the effective volume of a theoretical plate and the square root of the number of plates in the column. In our terminology, the definition is

$$v_n \leqslant 0.5 \frac{Lxs}{\sqrt{n}} (\varkappa + \Gamma\varkappa_1), \quad (7)$$

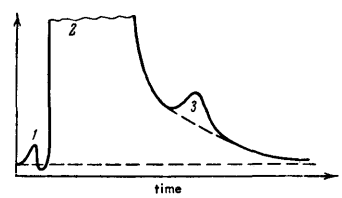


Fig. 2. Measurement of the area of an incompletely resolved impurity peak:
1) air; 2) main component; 3) impurity.

where s is the cross-sectional area of the column and n is the number of theoretical plates. Some simple manipulation gives

$$v_p \ll \frac{\omega_{0.5}}{4.7} \quad (8)$$

and

$$c_{max} \leqslant \frac{c_p}{5}, \quad (9)$$

where $\omega_{0.5}$ is the half-width of the peak, measure in millilitres of carrier gas, c_p the concentration of the desired constituent in the sample, and c_{max} the concentration of the same constituent at the maximum of the eluted peak.

These considerations show that a larger sample is permissible when the substance being analysed is strongly adsorbed. The size of the sample can also be increased in direct proportion to the cross-section of the column and to the square root of the column length.

Klinkenberg[6] has shown that the column can be overloaded by the volume of sample in the vapour phase (excluding the carrier gas) in addition to the type of overloading described by Eqn. (7), in which the volume of sample in the vapour phase includes the volume of the carrier gas. In the former case the permissible sample size can be calculated by replacing the factor 0.5 in Eqn. (7) by the factor 0.02.

Slight overloading of the column is sometimes beneficial, since it raises the sensitivity without appreciably degrading the resolution. A fourfold increase in the length of the column doubles the permissible sample size, the peak widths, and the peak separation, but leaves unchanged the concentrations of the constituents at the peak maxima. An amount of overloading which lowers the separation criterion to 1 whilst raising the concentration of the constituents at the peak maximum is therefore entirely acceptable.

Zhukhovitskii and Turkel'taub[7] have recently propounded the technique of step chromatography, in which large samples are used to give a stepped elution curve. The height of each step measures the concentration of the appropriate constituent.

If the time allowed for the separation is fixed, and the rate of mass-transfer is limited by internal diffusion, the peak width becomes proportional to the velocity of the carrier gas. Since

$$\mu_{0.5} = 3.33(\varkappa + \Gamma\varkappa_1)\sqrt{\frac{DL\varkappa}{\alpha}}, \quad (10)$$

it follows that $\mu \simeq \alpha$ if $2D\varkappa/\alpha$ is replaced by $C\alpha$ and L is replaced by $t\alpha/(\varkappa + \Gamma\varkappa_1)$, where t is the analysis time and C is a term which characterises mass transfer by internal diffusion. Hence a larger sample can be used if the gas velocity and the length of the column are increased. If the sample size is also increased in proportion to the flow rate the concentration at the peak maximum remains unchanged, because the diffuseness of the peak is proportional to the flow rate. Since the width of the chromatographic peak is proportional to time, the peak areas and the peak separation criterion also remain the same. It follows that the degree of separation can be adversely affected by column overload if the time of analysis is fixed.

Impurity Accumulation

Sorption on the stationary phase decreases the volume of an injected sample (concentration of desired constituent = c_p) by a factor of $\Gamma_0 = \varkappa + \Gamma\varkappa_1$, and raises the concentration correspondingly. During the subsequent elution on account of the diffuseness of the chromatographic band the concentration at the peak maximum, c_{max}, is inversely proportional to the square root of the column length (assuming no overloading), and at the column outlet the peak concentration is given by

$$c_{max} = p\frac{c_p\Gamma_0}{\sqrt{L}}, \quad (11)$$

where p is a proportionality coefficient. Desorption widens the peak by a factor Γ_0, and correspondingly lowers the concentration:

$$c_{max} = p\frac{c_p}{\sqrt{L}}. \quad (12)$$

In trace analysis these concentrations are frequently too low to be measured even if the column is overloaded with sample, when the value of c_{max} decreases slowly with L. Various methods of concentrating the impurity have therefore been devised. Thus, it is important to choose a packing on which the major constituent is adsorbed much more strongly than the impurity ($\Gamma_0^1 > \Gamma_0$). This compresses the injected sample by a factor Γ_0^1 and increases the concentration of both the main constituent and the impurity by the same factor. After elution, therefore, the latter concentration takes the value

$$c_{max} = p\frac{c_p}{\sqrt{L}}\frac{\Gamma_0^1}{\Gamma_0}. \quad (13)$$

This method has been used by one of us[8] in the analysis of volatile impurities in ethylene.

In the case of impurities of low volatility, adsorption is allowed to occur at some low temperature, T_1. This compresses the band by a factor $\Gamma_0(T_1)$. After removal of the major constituent, chromatography is carried out at a higher temperature T_2, resulting in an increase in the eluate concentration by a factor $\Gamma_0(T_1)/\Gamma_0(T_2)$. The low-temperature sorption can be carried out in a separate tube or on the column itself.

It is frequently possible to concentrate the impurity by partially or completely condensing out the main constituent in a suitable cold trap. This can be empty, or filled with a solid packing or with a liquid. As a result, the impurity concentration rises by a factor of $1/(1 + mC)$, where C is the initial fractional concentration of the main constituent and m is the fraction condensed. Removal of the main constituent improves the separation (by decreasing φ) as well as raising the concentration of the trace constituent.

Chromatograms free from the major peak have also been obtained by chemically removing the main constituent before the column, within the column itself, or beyond the column, by using the main constituent as carrier gas, or by choosing a detector insensitive to the main constituent.

All these techniques are effectively single-stage methods of enrichment of the impurity in the sample. Multi-stage enrichment is achieved in chromathermography[9-11], a technique which offers practically limitless possibilities in many problems of trace analysis. The programmed-temperature method[12] is suitable for continuously monitoring industrial processes, and enables low-volatility impurities to be detected in such a way that the main constituents do not give peaks on the chromatogram.

Clearly, the procedures discussed above have to be combined with analytical techniques suitable for multicomponent systems when it is desired to estimate trace impurities in complex mixtures.

Quantitative Interpretation of the Chromatograms

The main requirement on a method for the quantitative interpretation of trace-impurity chromatograms is that it should be capable of absolute calibration (carried out by calculations based on some experimentally found relationship between the concentration of the impurity and the response of the detector).

Internal standards are hardly ever applicable owing to the difficulty of preparing a series of standard mixtures with a very low concentration of one constituent. The internal normalisation method is likewise unsuitable because of its low precision, even in cases where the main peak can be fully plotted on the chromatogram.

When the peaks are sufficiently well resolved, the peak height h is the parameter normally used. In cases of partial resolution it is better to use the peak area as a measure of concentration, taking the precaution[13] of using the extrapolation of the main peak as a corrected base line (see Fig. 2).

3. TRACE IMPURITY ANALYSIS WITH LARGE SAMPLES

Isothermal Separation of Large Samples

As stated above, the sensitivity of the method can often be raised by overloading the column with sample. Many authors have analysed trace impurities simply by using rather large samples, which they eluted under isothermal conditions. Pietsch[14,15] was among the first to use this approach in his work on the determination of oxygen, carbon monoxide, nitrogen, and light hydrocarbon impurities in commercial and in pure ethylene. A conventional

TABLE 1. Trace impurity analysis by isothermal separation of large samples.

Desired impurity	Main constituent	Length of column. Sorbent	Detector	Carrier gas	Temperature, °C	Sample size	Sensitivity, %	References
Propane, propylene, C_4 hydrocarbons	ethylene	8 m. Triisobutylene on Celite	katharometer	hydrogen	25	5 ml gas	5×10^{-3} wt. 5×10^{-3} wt. $5 \cdot 10^{-2}$ wt.	16
Hydrogen, oxygen, nitrogen, methane, carbon monoxide	ethylene	2 m. Molecular sieve 13X	katharometer	helium	25	25 ml gas	5×10^{-4} vol. 4×10^{-4} wt. 7×10^{-4} wt. 7×10^{-4} wt. 10^{-3} wt.	16
$C_2 - C_4$ hydrocarbons, carbon dioxide	methane	mixture of triisobutylene and transformer oil on C-22 support	thermistor katharometer	hydrogen	0	–	$10^{-3} - 5 \times 10^{-3}$	17
Methylacetylene, vinylacetylene	acetylene	1 – 3.5 m. Dibutyl phthalate on fire brick	thermistor katharometer (thermochemical)	hydrogen, air	20 – 50	50 – 100 ml gas	$< 10^{-2}$	18
Propadiene	propylene	2 m. Glycol solution of silver nitrate on C-22	katharometer	helium	25	25 ml gas	5×10^{-4}	19
Isopropanol	benzene	1.2 – 2 m. "Nujol"* on "Celite"**	thermistor katharometer	helium	64	10 μl liquid	$< 10^{-4}$ wt.	20
Benzene	toluene	1.2 – 2 m. Tetraethylene glycol dimethyl ether on "Celite"	thermistor katharometer	helium	64	20 μl liquid	$< 10^{-3}$ wt.	20
Cyclohexanol	toluene	1.2 – 2 m. "Carbowax"*** and sorbitol on Celite	thermistor katharometer	helium	155	10 μl liquid	4×10^{-4} wt.	20
Methanol	water	1.2 – 2 m. "Carbowax" on "Celite"	thermistor katharometer	helium	80	10 μl liquid	2×10^{-4} wt.	20
Methane, ethane	air	carbon	interferometer and volumetric gas analyser	air	20 – 30	–	6×10^{-3} vol. calculated as CO_2	21
Carbon oxide sulphide	natural gas	3.6 m. *N,N*-Dibutylacetamide on a special support	katharometer	helium	28	50 ml gas	2.5×10^{-3}	22
Hydrogen, nitrogen, carbon monoxide, $C_1 - C_4$ hydrocarbons	ethylene	two columns, 0.6 and 3 m long. KSM silica gel. Crossover of gas flow	katharometer thermistor katharometer	air	room temperature for volatile constituents, programmed to 250° for heavier constituents	1 litre gas	2×10^{-4} 5×10^{-2} 1.5×10^{-3} 1.5×10^{-3}	23

* Petroleum jelly (Ed. of Translation).

** Preformed catalyst carrier made by Johns-Manville USA (Ed. of Translation).

*** Polyethylene glycols and methoxypolyethylene glycols made by Union Carbide Corp. (Ed. of Translation).

katharometer, and sometimes even a nitrometer filled with alkali, proved adequate as detectors in this work.

The most significant results obtained by isothermal separation of large samples are summarised in Table 1. It seems clear that, with a large enough sample and a katharometer detector, the sensitivity can reach 10^{-4}%. This level of sensitivity is adequate in many practical problems, but it represents the ultimate limit of katharometer response and cannot be further improved by increasing the sample size.

Since the loss of separation efficiency is one of the factors which set an upper limit to the permissible sample size in chromatographic trace analysis — particularly at high values of φ, *vide* Eqn. (2) — the advantage of using the main constituent as carrier gas is obvious: the major peak disappears, and the impurity peak becomes unmistakable. This device was used by Turkel'taub[21] in what appears to be the first application of chromatography to trace impurity analysis, and enabled him to determine methane and ethane in air with a sensitivity of approximately 10^{-5}%.

Wilkins and Wilson[24] achieved a sensitivity of 5×10^{-4}% in their estimation of oxygen, nitrogen, and other gaseous impurities in helium by using pure helium as carrier gas.

Obviously, when using a katharometer, the main peak can be eliminated by choosing a carrier (a single gas or a mixture of gases) of very nearly the same thermal conductivity as the main constituent.

Elimination of the Main Constituent

The techniques discussed so far offer a slight improvement in the sharpness of separation of the peak. However, if the main constituent is physically removed from the sample to be analysed, the sample volume can be drastically decreased, with a corresponding enrichment of the trace impurity. This raises the sensitivity of the method by compressing the peaks as well as by lowering the value of φ.

Ray[25,26] achieved a remarkable concentration of non-olefinic impurities in ethylene by passing the gas over

TABLE 2. Trace impurity analysis after elimination of the major constituent.

Desired impurity	Main constituent	Method of separation	Length of column, Sorbent	Detector	Carrier gas	Condensation temperature, °C	Analysis temperature, °C	Sample size	Sensitivity, %	References
Methane	air	99% of the air vented to atmosphere after first section	0.6 m + 1.2 m. Carbon with 1.5% dinonyl phthalate	katharometer	helium	–	room	20 ml gas	5×10^{-4}	32
Carbon dioxide, hydrocarbons up to C_4	liquid oxygen	impurities frozen out	benzyl benzoate and silicone oil on a support	katharometer	–	liquid oxygen	room	–	10^{-7} – 10^{-8}	33
Hydrocarbons up to C_4	synthetic gas	impurities frozen out in a carbon trap	1.5 m. Triisobutylene on "Meka" support. Solution of silver nitrate in benzyl cyanide on "Meka" support	nitrometer, katharometer	carbon dioxide	75. Desorption at 150°	room	up to 10 litres gas	10^{-3}	34
Hydrogen, oxygen, methane, carbon monoxide	carbon dioxide	main constituent frozen out	molecular sieves 5A and 13X	katharometer	argon, helium	– 196	50	–	10^{-4}	35
$C_5 - C_{10}$ hydrocarbons	cracking gas	circulating system. Liquid samples taken from condensation trap	3.5 m. Silicone elastomer on "Celite"	katharometer	hydrogen	dry ice	86	6.6 litres gas	0.1 mg × × litre^{-1}	38
$C_1 - C_4$ aldehydes, $C_3 - C_4$ ketones, $C_2 - C_6$ hydrocarbons	white medicinal paraffin	impurities distilled into a cold trap from sample at 60°	2 m. Mixture of silicone and dicyandiethyl oxide on a support	flame ionisation	nitrogen	liquid air	20	10 g	10^{-7} wt.	43
Ethyl methyl ketone, toluene	waxes, lubricating oils	sample heated to 200° in a stream of helium and impurities frozen out	3 m. "Carbowax" on C-22	katharometer	helium	– 50. Desorption at 125°	100	10 g	5×10^{-2} – 10^{-3}	44
Hydocyanic acid	water	water equilibrated with air and impurity condensed out	5.4 m. Dinonyl phthalate on "Chromosorb"*	thermistor katharometer	helium	acetone – dry ice mixtures	57	up to 10 litres gas	10^{-4} – 10^{-6} mole	45
Carbon dioxide, in sodium carbonate	water	carbon dioxide evolved with hydrochloric acid	30 cm. Silica gel	thermistor katharometer	helium	–	room	30 g	2×10^{-3}	46
Carbon	iron	combustion in a stream of oxygen	silica gel, "Alusil"	photometric cell	oxygen	–	room	0.01 g	10^{-6}	47

* Graded, calcined diatomite aggregates made by Johns-Manville, USA (Ed. of Translation).

carbon, saturated with bromine, in the inlet section of his chromatographic column.

Various classes of compounds can be eliminated by using methods developed for the chromatographic analysis of complex mixtures. Thus, unsaturated compounds can be removed by elution through a section containing silica gel saturated with sulphuric acid[27], normal hydrocarbons[28-30] by 5 Å molecular sieves, alcohols by a polyester column[31]. All these methods can obviously be applied in trace analysis.

Cold traps have been widely used for separating impurities from the major constituent. According to their relative volatilities, either the impurities[32-34] or the main constituents[35] can be frozen out.

West *et al.* have developed a technique for concentrating impurities in air[36], using a charcoal trap, which gives a sensitivity of 10^{-3}–10^{-4}% with samples of the order of 20 litres. The concentrated impurities are vaporised and injected into the chromatographic column by rapidly raising the temperature of the cooled trap.

Mackay[37] has investigated the condensation of impurities in a specially designed apparatus.

Vigdergauz and Gol'bert[38,39] estimated high molecular weight impurities in cracking gas by absorbing them in a cold trap containing n-octane (which they used as an internal standard). The gas was circulated through the cold trap, from which a liquid sample was then extracted and analysed. Hydrocarbons in the range C_6–C_{10} were determined with a sensitivity of approximately 0.1 mg litre^{-1}.

Serpinet[40], and also Vyakhirev *et al.*[41], used preparative gas chromatography techniques to isolate the impurities before identifying and estimating them.

TABLE 3. Trace impurity analysis with thermal enrichment in the column.

Desired impurity	Main constituent	Length of column. Sorbent	Detector	Sorption temperature, °C	Analysis temperature, °C	Sample size	Sensitivity, %	Carrier gas	References
Methane	air	1st section 0.6 m, 2nd section 1.2 m. Carbon with 1.5% dinonyl phthalate	katharometer	– 78	room	10 ml gas	$< 10^{-4}$	helium	32
C_4 and higher hydrocarbons, halogen derivatives	chloroethylene	3 m. "Nujol" on C-22	katharometer	liquid nitrogen	30	1 ml liquid	$< 10^{-4}$	nitrogen, helium	48
C_2 – C_5 hydrocarbons	liquid air	7.6 m. Dimethylsulpholane on C-22	katharometer	liquid nitrogen	0	up to 10 litres gas	up to 10^{-6}	helium	49
C_2 – C_5 hydrocarbons	air, exhaust gases	0.3 m + 7.6 m. Dimethylsulpholane on brick	katharometer	liquid nitrogen	0	up to 10 litres gas	5×10^{-6}	helium	50
Carbon monoxide, hydrogen, C_1 – C_4 hydrocarbons	ethylene	5 m alumina, 1 m dibutyl phthalate on diatomite	thermochemical	room, increasing to 130°	2nd section at room temperature	20 ml gas	5×10^{-3}	air	51
Light gases and C_2 – C_5 hydrocarbons	–	7.5 m carbon, 15 m dimethylsulpholane on brick	katharometer	liquid nitrogen	20	10 ml gas	9×10^{-3}	helium	53
Carbon dioxide	air	2 m silica gel	katharometer	– 80	–	500 ml gas	2×10^{-8}	helium	54
Acetylene	air, oxygen	2 m silica gel	katharometer	– 80	50	10 litres gas	1.3×10^{-8}	helium	54
Nitrogen, oxygen, methane, carbon monoxide	hydrogen	silica gel (50 cm³). 2 m molecular sieve 5A	katharometer	– 80	50	1 litre gas	10^{-4}	helium	54
Methane, ethane, carbon dioxide, ethylene, C_3 hydrocarbons	hydrogen	2 m silica gel	katharometer	– 80	50	20 litres gas	5×10^{-6} – 10^{-5}	helium	54
C_3 – C_5 hydrocarbons	hydrogen	polyethylene glycol on "Chromosorb" (50 cm³). 4 m dimethylsulpholane	katharometer	– 80	50	–	10^{-4}	helium	54
Acetylene	ethylene	polyethylene glycol on "Chromosorb" (50 cm³). 4 m dimethylsulpholane	katharometer	– 80	– 25	40 litres gas	10^{-4}	helium	54
C_1 – C_2 and higher hydrocarbons	air, methane	"Alusil"	colorimetric	50	60 – 120	200 ml gas	10^{-6} – 10^{-7}	oxygen	56
Carbon monoxide	hydrogen	0.35 m carbon, 0.3 m silica gel	katharometer, with conversion into CO_2 between columns	– 75 – 45	50	7 litres gas	10^{-7}	nitrogen	55

Light impurities in substances of low volatility (such as lubricating oils) are usually determined by evaporating them from the sample, concentrating them in a trap, and introducing them into the column after a second evaporation.

Impurities which lower the flash-point of lubricating oils can be estimated by an interesting chromatographic method[42] which is far more general and precise than the conventional flash-point measurements.

Typical results of various methods of trace analysis (involving elimination of the main constituent) are summarised in Table 2.

Enrichment as a Result of Thermal Effects on the Column

In the opening section it was pointed out that thermal effects can be very significant since they enable the impurities to be concentrated, thus raising the sensitivity of the analytical method.

Several workers have used methods involving low-temperature adsorption of the sample on the column itself or on to an auxiliary section, followed by chromatographic separation at a higher temperature. The main results, set out in Table 3, show that a sensitivity of the order of 10^{-7}% can be achieved with large enough samples (several litres). In another paper[57] the separation of impurities in air at low temperatures is discussed.

Many publications dealing with the chromathermographic method of trace impurity analysis have appeared. Thus, Vagin *et al.*[58] have described a chromatographic method of analysis of carbon dioxide in oxygen, in amounts of $2.5 \times \times 10^{-5}$ vol.%, using sample volumes of up to 50 litres and a low-sensitivity detector (a GEUK-21 gauge).

Zhukhovitskii and Turkel'taub[59] constructed a recirculating chromathermographic apparatus, consisting of two columns and a detector, in which sample volume and degree of enrichment can both be increased at will.

Petukhov and Vagin[60] determined heavy noble gases and methane impurities on a continuous basis in their programmed-temperature apparatus. The chromathermographic KhTD apparatus, now commercially available, can make continuous analyses of complex mixtures and of trace impurities in various materials.

4. TRACE IMPURITY ANALYSIS WITH HIGH-SENSITIVITY DETECTORS

High-sensitivity detectors, based on the measurement of ionisation currents in the material under investigation, have become very popular in the last five years. Lovelock[61-66] has described several forms of a detector in which a radioactive source is used to ionise the gas. McWilliam and Dewar[67,68] made a detector in which the various constituents are ionised by being burned in a hydrogen flame. Detectors of this type offer a sensitivity of the order of $10^{-12}-10^{-14}$ mole.

These modern detectors, with their impressive performance, offer obvious advantages in the development of analytical methods for trace amounts of various substances. Chromatographic apparatus incorporating ionisation detectors are now available from a number of firms in the USA, England, West Germany, and other countries.

Table 4 summarises the main analytical results for trace impurities obtained with ionisation detectors. The most striking feature of this work is the achievement of sensitivities of the order of $10^{-4}-10^{-5}$% with relatively small samples.

Still higher sensitivities are possible if a high-sensitivity detector is used in conjunction with one of the enrichment methods discussed above. Thus, Theer has shown[78] that the detection for sensitivity hydrocarbon impurities in air with a flame-ionisation detector can be improved from 5×10^{-6} (1 ml sample) to 10^{-8}% by increasing the sample volume to 50–100 ml and carrying out a preliminary enrichment on a silica gel column at -78°.

Since ionisation detectors are insensitive (or only slightly sensitive) towards certain substances, it is possible to lower the value of φ [see Eqn. (2)] and obtain a sharper separation by working under conditions where the detector does not respond to the major constituent. Turkel'taub *et al.*[79] took advantage of this phenomenon in their work on the analysis of traces of benzene in silicon tetrachloride, using an apparatus with a flame-ionisation detector. Shima[80], and Emery and Koerner[81], who estimated phenols and fatty acids, respectively, in aqueous solutions, resorted to the same stratagem.

Various procedures for increasing the sensitivity of ionisation detectors towards permanent gases have been suggested. In one of these[82] helium is used instead of argon as the carrier gas: this enables oxygen, argon, and other gases to be ionised in the detector and to be estimated with a sensitivity of approximately 10^{-4}%. Other methods[83-85] rely on the introduction into the argon stream of quite small amounts of organic substances, able to increase greatly the ionisation of various molecules.

Some selective, high-sensitivity detectors have also been described: the emissivity detector and the electron affinity detector[86,87]. These react very strongly towards certain classes of compounds (aromatic hydrocarbons, in particular), but have only a moderate sensitivity towards other substances. They are thus eminently suited to the detection of impurities (*e.g.* aromatic substances in aliphatic hydrocarbons), since they give a low value of φ as well as a high sensitivity.

5. DETERMINATION OF TRACE IMPURITIES IN COMPLEX MIXTURES

The analysis of trace impurities in multicomponent systems is complicated by the serious overlapping of the peaks due to impurities with those due to the main constituents. Trace-impurity techniques therefore have to be modified, and combined with methods of analysis worked out for complex mixtures.

Heuschkel *et al.*[88], for example, have developed a chromatographic method of analysis of very small amounts (approximately 5×10^{-4}%) of propadiene and methylacetylene in a propane–propylene fraction containing up to 0.5% of C_4 hydrocarbons. A two-stage separation was used, with a silicone oil column and a diethylformamide column (both stationary phases were supported on "Sterchamol" brick). The fractions obtained after the first stage were collected in a cold trap, which was used as a sample injector for the second stage.

Vigdergauz, Gol'bert, and their coworkers[89,90] developed a method of analysis of acetylene, methylacetylene, ethyl-

TABLE 4. Trace impurity analysis with high-sensitivity detectors.

Desired impurity	Main constituent	Length of column. Sorbent	Detector	Carrier gas	Temperature, °C	Sample size	Sensitivity, %	References
Acetylene	nitrogen, ethane, propylene	6 or 12 m. Dimethylsulpholane on brick	argon ionisation	argon	10 – 20	10 – 20 ml	5×10^{-4}	69
Hydrocarbons	exhaust gases	0.2 m. Silica gel	flame ionisation	hydrogen	room	1 – 10 ml	10^{-7}	70
$C_1 - C_6$ hydrocarbons	air	2 columns in parallel, up to 4 m long, with dimethylsulpholane and diisodecyl phthalate on brick	flame ionisation	nitrogen – hydrogen mixture	25	1 ml	10^{-4}	71
Acetylene	ethylene	1.6 m. Hexamethylphosphoramide on brick	flame ionisation	–	27	5 ml	3×10^{-6}	72
Acetylene	ethylene	2.7 m. Dekalin on "Sterchamol" brick	flame ionisation	nitrogen	0	25 ml	10^{-6}	73
Carbon dioxide, carbon monoxide	ethylene	1 m. Carbon	flame ionisation (following conversion into methane)	hydrogen	room	25 ml	10^{-4}	74
Propylene	ethylene	mixture of ethanolamine, ammonium nitrate, and copper oxide on "Sterchamol" brick	flame ionisation	hydrogen	room	10 ml	3×10^{-3}	74
$C_8 - C_{10}$ aromatic hydrocarbons	styrene	capillaries: 61 m with "Apiezon" and 78 m with "Ucon"	argon triode	argon	70 – 100	0.005 μl	5×10^{-4}	75
Carbon oxide sulphide	carbon dioxide	1.2 m. Silica gel	argon ionisation	argon	25	115 ml	3×10^{-5}	76
Acenaphthene in onion root tips	–	0.15 m. Silicone oil on brick	flame ionisation	hydrogen	183	20 μl of tetralin solution	0.2γ	77
$C_2 - C_6$ hydrocarbons	air and oxygen	2 m. "Alusil" or silica gel	flame ionisation	hydrogen	room	1 ml	5×10^{-6}	78
Benzene	silicon tetrachloride	2 m. Liquid paraffin on engineering brick	flame ionisation	hydrogen	25	–	3×10^{-4}	79
Oxygen, hydrogen, nitrogen, methane	–	molecular sieve MA	argon ionisation	argon + $+ 10^{-4}$ % ethylene or acetylene	room	–	$10^{-4} - 5 \times 10^{-6}$	83
Oxygen, hydrogen, methane, argon, carbon monoxide	–	0.3 m. Molecular sieve 5 Å	argon ionisation	helium	room, but oxygen and argon separated at – 80°	–	10^{-12} mole per 1 ml carrier gas	82
Oxygen, hydrogen, nitrogen, methane, carbon monoxide	–	molecular sieve 5 Å	argon ionisation	argon + + trichloroethylene	room	–	10^{-5} ml	84

acetylene, propadiene, and divinyl in cracking gas and its fractions. A two-stage separation was again necessary, using columns packed with diisobutyl phthalate and sulpholane† (or dimethylsulpholane) respectively, supported on crushed brick. Narrow fractions were taken from the first column and injected into the second column without being first condensed out.

In conclusion we should point out that gas chromatography is not confined to the laboratory-scale analysis of trace impurities: some existing assemblies can be inserted in the control loop of technological processes[91].

† Tetrahydrothiophene 1,1-dioxide (Ed. of Translation).

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