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CONCENTRATION OF TRACE AMOUNTS OF IMPURITIES BY PREPARATIVE GAS CHROMATOGRAPHY

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SUMMARY

Some methods are proposed for the improved concentration of impurities from complex mixtures prior to analysis. The introduction of impulse of solvent increases the condensation of the impurities in the traps.

The use of gas chromatography (GC) for resolving mixtures enables bands of separated components to be obtained at the column outlet, from which bands the components can be isolated and collected, provided that their concentration is adequate.

In preparative GC, in order to facilitate the collection of components present in low concentrations, large sample volumes, low-temperature cooling of the traps, filling the traps with adsorbents, electrostatic precipitators, etc., are used¹. Under these conditions, however, it is very difficult in practice to trap components that are present in concentrations below 0.1 %.

For analytical purposes, in particular for identification, it is not always necessary to isolate the trace component, as it may suffice to raise its concentration to the sensitivity level of the identification method being used. For this purpose, preparative-scale chromatography can be used in two versions².

The first procedure involves trapping the total amount of impurities before or after the main component, with sampling according to elution time, without the use of detection, as one is generally faced with the problem of raising the concentration of impurities that are not recorded by the detector under these conditions. This method is suitable, for example, for concentrating impurities from alcohol-water mixtures (Fig. 1).

The other procedure facilitates the improved isolation of the impurity by superimposing on the band of the impurity the band of some other easily condensable substance. In this instance, the admixture is captured within the volume of the gas space of the trap by the solvent introduced, and a combination of the condensation of the substances and of the trace impurity is effected.

If, as the condensing agent, the same main component is used from which the admixture is isolated, then with various volumes of the sample introduced a concentration effect is produced.

The superimposition of the bands of the condensed and condensing agents can be achieved in a variety of ways. The simplest is the overflowing impulse method,

which involves the introduction during one cycle of a large and small (additional) portion of the original mixture. Depending on the location on the chromatogram of the admixture in question relative to the main component, the additional portion is introduced either before or after the introduction of the principal, large portion of the sample from which the concentration is made (Fig. 2).

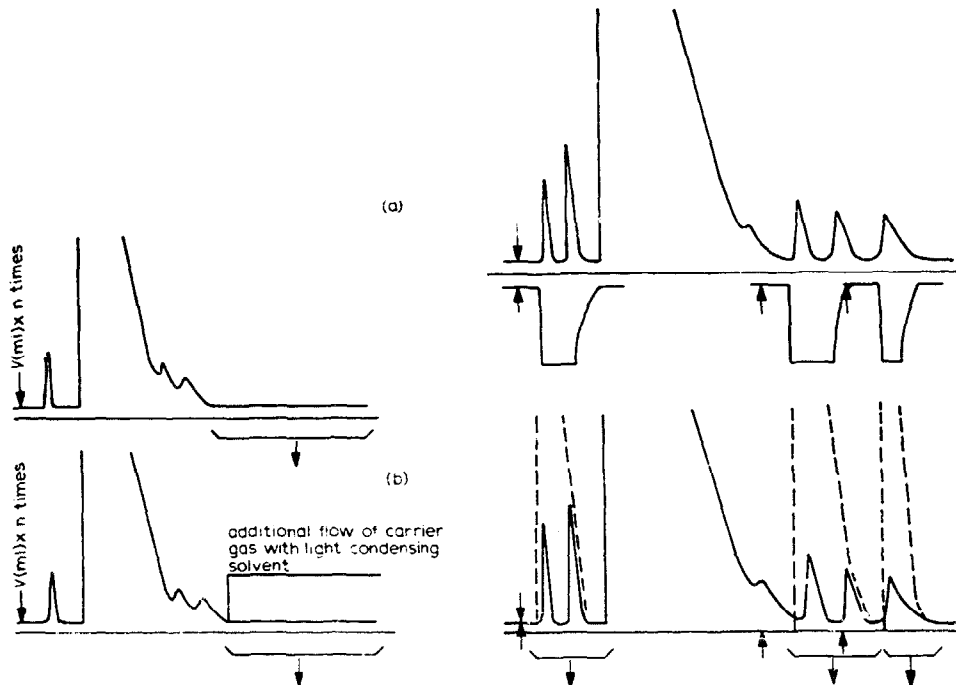


Fig. 1. General principles of concentration of impurities by preparative chromatography, by (a) simple condensation and (b) condensation with additional flow.

Fig. 2. General principle of concentration by the capture method.

As an example, the impurities in toluene, with a total content of eight impurities amounting to 0.7 %, were concentrated on an "Etalon 1" preparative chromatograph. The analytical chromatogram of toluene is shown in Fig. 3. The separation (preparative-scale GC) was carried out on polyethylene glycol adipate coated at a level of 25 % on a Spherochrom-1 support (0.5-1 mm fraction). The column was 30 mm I.D. and 3.2 m long; the thermostat temperature was 75 °, the vaporizer temperature 140 °; and the carrier gas flow-rate was 500 ml/min.

Prior to the concentration step, preparative chromatograms had been obtained separately for toluene sample volumes of 20 ml and 2 ml. Then the chromatogram of the small portion of the sample was superimposed on the chromatogram of the large portion on a similar time scale in such a way that the beginning of the elution of the main component of the small portion coincided with the elution of the impurity to be concentrated from the large portion. The zone of the impurity was completely covered by the main component of the small portion of the sample. From the superimposition, the time of shift of the origin of the chromatogram was determined, which

corresponded to the required difference in the introduction times of the large and small portions. The combined chromatogram is shown in Fig. 4.

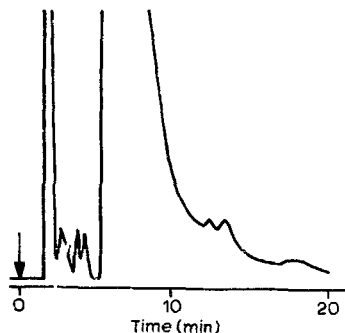


Fig. 3. Chromatogram of the initial sample of chemically pure grade toluene. Conditions of analysis (analytical GC): polyphenyl ester, 15% on Celite 545; column length 3 m; temperature 75° ; $t_{\text{evaporator}} = 170^{\circ}$; flow-rate = 50 ml/min; $V = 1 \mu\text{l}$.

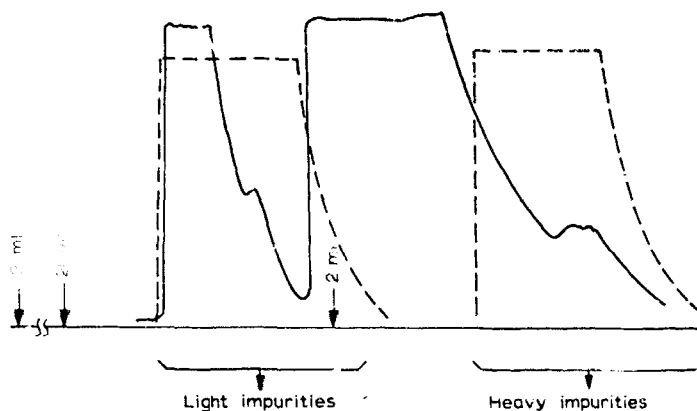


Fig. 4. Preparative chromatogram of superimposition in concentrating the "front" and "tail" peaks with the introduction of two additional portions. Solid line, chromatogram of the main portion, 20 ml; broken line, chromatogram of the additional portions of chromatographically pure toluene, 2 ml.

The concentration was effected by the consecutive introduction first of 2 ml and then of 20 ml. The difference in the times of introduction in the instance considered was 15 min. The traps for collecting the admixture concentrates were switched on for the time of elution of the main component of the additional portion of the sample. During the remaining time, a discharge trap or a trap for the main component was operated. When the traps were cooled with water at 15° , the output of concentrate was 0.5 ml, and of toluene 12–14 ml. The chromatograms of the products collected are shown in Fig. 5. From a comparison of Figs. 2 and 5, it is evident that the concentration of impurities in toluene has increased. In addition to this concentration effect, a chromatographically pure product from the main portion was obtained.

To concentrate impurities eluted after the main component, the superimposition of chromatograms is carried out as shown in Fig. 4, *i.e.*, the additional portion is

introduced after the main portion. The chromatogram of the concentrate obtained is shown in Fig. 5b, which shows that the content of the "tail" admixtures has increased, while the "front" admixtures are absent. The output of the concentrate and of toluene remained about the same.

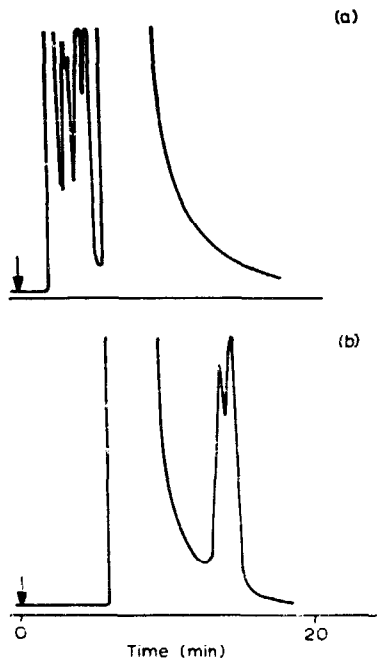


Fig. 5. (a) Chromatogram of the concentrate of impurities eluted before the main component and of the toluene of the main fraction. (b) Chromatogram of the concentrate of impurities eluted after the main component. For conditions of separation, see Fig. 3.

The introduction of two or more additional portions, before and after the introduction of the main sample, enables the concentrates of advancing and "tailing" admixtures to be obtained separately from a single sample; it is possible to concentrate separately each impurity. To achieve this it is necessary to shift the time of introduction of the additional portions in accordance with the time of elution of the impurities. The method is also applicable to admixtures obscured by the "tail" of the main component.

An important variable for this concentration is the difference in the volumes of the large and small portions. The greater the difference, the smaller is the volume into which the admixture is concentrated, and the greater is the effect of the concentration.

Provided that complete condensation of the main component of the additional portion is achieved, the enrichment coefficient should be equal to the ratio of the volumes of the main and the additional portions. With incomplete condensation, the coefficient may be greater than this ratio, *i.e.*, concentration takes place in a smaller volume of the condensing component introduced, and the effect of concentration can be increased by more than two to four times with a constant ratio of the volumes of the portions introduced.

In the case considered here, the maximum enrichment coefficient was 20 with a ratio of the portions introduced equal to 10. For most of the impurities, the enrichment coefficient was greater than 10, which may be partially explained by an incomplete, partial condensation of the toluene of the additional portion and by easier conditions of condensation of the impurities.

It was found that the concentration of trace impurities present in a substance in tenths and hundredths of one per cent can be achieved.

If the concentrate obtained is repeatedly introduced into the chromatograph, as the main portion of the sample, then on the introduction of the additional portion the effect of concentration will accordingly increase and reach 100–200 relative to the initial mixture. Fig. 6 is an example of this repeated concentration with a ratio of the volumes of the portions introduced equal to 4.

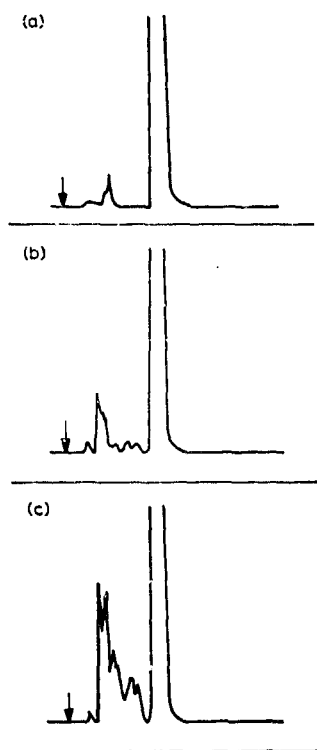


Fig. 6. Chromatogram of toluene: (a) original; (b) after the first concentration; (c) after repeated concentration.

As the condensing agent, any substance can be used for which it is desirable and possible to carry out identification in subsequent work.

REFERENCES

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- 2 I. P. OGLOPINA AND E. G. NIKITIN, *U.S.S.R. Pat*, 1,474,936, Issued 10.9.1971, Appl. 20.8.70.