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Note

Concentration of trace components by the heat-dynamic method using a built-in accumulator

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Concentration techniques are widely used to increase the sensitivity of analytical determinations, and make it possible to determine trace impurities at very low concentrations without increasing the sensitivity of the detection as such[1–3].

The most effective dynamic concentration method is a thermal chromatographic technique, especially in the form of the heat-dynamic technique suggested by Zhukhovitsky and Turkeltaub[4]. The basis of the heat-dynamic method is that a furnac with a negative temperature gradient is periodically moved along the column-concentrator in which the sample is continuously introduced to. Under the influence of the thermal gradient the heavy impurities in the sample are adsorbed at the beginning of the column, then start to move along the column in the furnace zone and when they reach the end of the column they are removed. As a carrier gas is used, the main components of the sample must be lighter than the trace components of interest. Using this method it has been shown to be possible to determine organic substances in air at concentrations level down to 10^{-8}% by weight[5].

In practical applications of the heat-dynamic method at the trace level, some obstacles limit the degree of concentration degree possible and adversely affect the time of analysis, owing to the long duration of desorption and losses as a result of difficulties in heating the sorbent layer rapidly. In order to solve both of these problems and to make automatic analysis possible, a further version of the thermodynamic method is suggested here.

The basis of the suggested method is first the utilization of an accumulator where the bulking and storage of the concentrated impurities after several concentration cycles take place[6]. Second, a column of rectangular cross-section is used which, in comparison with a round column, allows a decrease in the heating rate and acceleration of the thermal field movement, hence avoiding considerable losses. The third feature of the unit is the use of an inert carrier gas.

EXPERIMENTAL AND RESULTS

Fig. 1 shows a simplified diagram of the unit. Desorption, concentration and transfer of the impurities from the concentrating part of the column into the accumulator is effected by the carrier gas (air) from a gas flask.
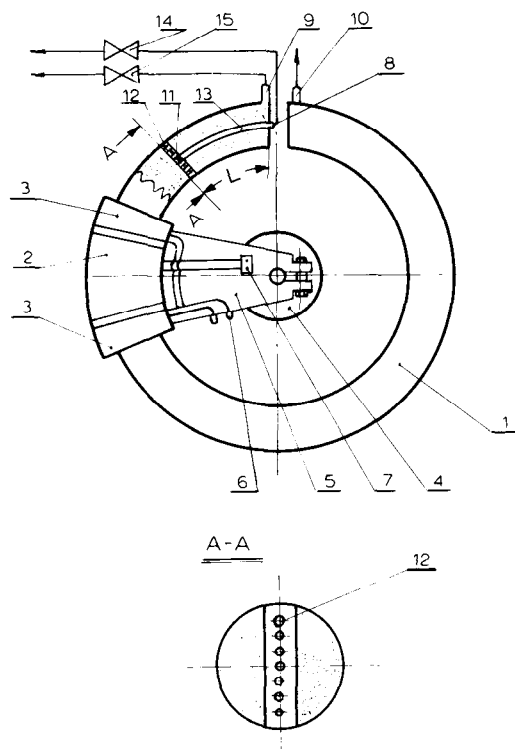
Fig. 1. Heat-dynamic unit with storage accumulator. 1, Flat, rectangular column of circlar shape; 2, moving furnace; 3, additional sections of the furnace (may be coolers); 4, motor for moving the furnace and coolers; 5, bracket; 6, connecting tube on the inlet and outlet of the coolant lines; 7, current supply to the furnace heaters; 8, connnecting tubes on the inlet of the sample and carrier gas lines; 9 and 10, connecting tubes on the carrier gas and concentrated trace outlet lines; 11 and 12, transfer tube with the lattice frame; 13, outlet tube; 14 and 15, valves on the carrier gas and concentrated trace outlet lines. A-A, cross-section; 12, lattice frame.

Mixtures of air and trace levels of benzene (Table I) were prepared by the dynamic method, a porous Teflon ampoule containing benzene being placed in thermostated cell through which air from the gas flask was continuously supplied at a constant velocity[2].

A 15-l volume of the sample mixture of air and benzene (Table I) with a velocity 50 ml/min, checked by a rotameter through the input 8, was introduced into the flat stainless-steel column of length 1 m and cross-section 20 × 5 mm filled with carbon black on Chromosorb W. The initial temperature of the column was 22°C and the desorption temperature measured in the sorbent zone was 250°C. Cooling water at 18°C was supplied to section 3. To provide a heat pulse in the accumulator for desorption of benzene the temperature was increased to 250°C for 2–3 sec.

The concentration procedure was as follows. The accumulator worked (*i.e.*, the gas flow moved through it) only when valve 1 was opened (Fig. 2). During the concentration the accumulator was disconnected from the gas flow which was leaving the concentrator through line 2. The procedure can be divided into several stages. At the beginning of the first stage, at the moment when the sample containing the trace
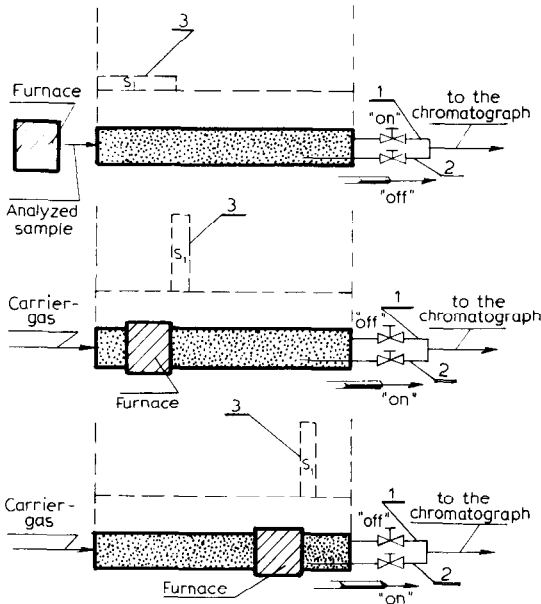
Fig. 2. First stage of the concentration. 1, Concentrated trace outlet line; 2, carrier gas flow line; 3, position of the concentrated zone.
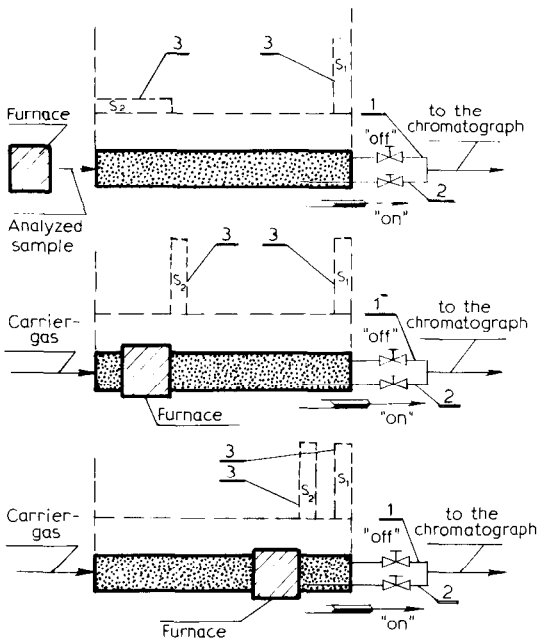

Fig. 3. Second stage of the concentration. 1, Concentrated trace outlet line; 2, carrier gas flow line; 3, position of the concentrated zones.
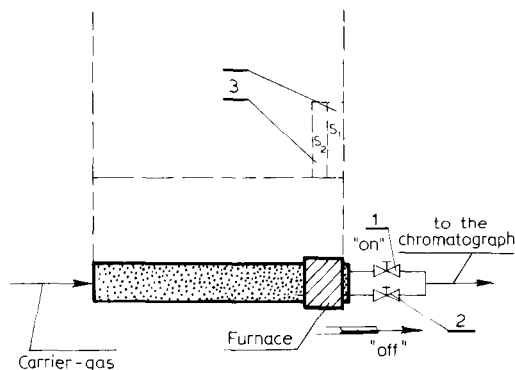
Fig. 4. Third stage of the concentration. 1, Concentrated trace outlet line; 2, carrier gas flow line; 3, position of the concentrated zones.

impurity in an amount S is introduced, valve 1 is in the "on" position and valve 2 in the "off" position. Then the heated furnace with the sections 3 (Fig. 1) cooled with water begins to move and transfer the concentration zone (Fig. 2). When the furnace reaches the accumulator valve 1 is closed and valve 2 is opened and the concentration zone is transported into the accumulator (at the same time the carrier gas continues to pass through line 2). This is illustrated at the middle and lower parts of Fig. 2. The oven is then returned to its initial position (out of the column) and the column is cooled to ambient temperature.

The second cycle is run in the same way, the only difference being that impurity from the first stage in an amount S has already been transferred into the accumulator (Fig. 3).

Fig. 4 shows the third stage of the elution of the trace components.

The benzene concentrated by the above procedure was analysed chromatographically (Table I), using an LKhM-8MD chromatograph with a flame-ionization detector.

A multi-column system with rapid heating and optimum cooling techniques are under investigation. The method may be generally applicable and could also be used in liquid chromatography.

TABLE I

CONCENTRATION OF BENZENE BY THE HEAT-DYNAMIC METHOD WITH AN ACCU-MULATOR

Sample No.	Benzene concentration in air sample before concentration (wt.-%)	No. of concentration cycles	Benzene concentration after the concentration cycles (wt.-%)	Loss (%)
1	$2.37 \cdot 10^{-2}$	4	$8.53 \cdot 10^{-2}$	10.03
2	$6.48 \cdot 10^{-4}$	2	$10.9 \cdot 10^{-4}$	15.2
3	$8.99 \cdot 10^{-3}$	3	$23.2 \cdot 10^{-3}$	13.8
4	$1.23 \cdot 10^{-4}$	7	$7.52 \cdot 10^{-4}$	11.5
5	$3.56 \cdot 10^{-4}$	5	$15.59 \cdot 10^{-4}$	12.4

CONCLUSIONS

The suggested method with a trace accumulator allows the concentration of organic compounds in gas and vapour mixtures to be increased and makes it possible to carry out the concentration process automatically.

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