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AUTOMATION OF CHROMATOGRAPHY OF RADIOACTIVE SUBSTANCES

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SUMMARY

A technique for the automation of the registration of data of a chromatographic separation of radioactive substances is described whereby a device is used for delivery of information to a punched tape. The results of computer processing of the data are shown for an actual example—the study of the influence of nuclear radiation on isotopic exchange in the gaseous phase.

Studies of radioactive substances and the use of radioactive methods for the solution of different scientific problems have led to a wide use of radiochromatography. Along with any necessary apparatus modifications the processing of analysis data is improved by using methods of computing. It is noteworthy that sometimes an autonomous computing system is preferable with gas chromatography[1,2].

The system of automation of chromatographic separation of radioactive substances described in this paper implies that there is a Universal Computer available. It consists of two stages: the automatic recording of the data in a discrete form followed by computer processing.

The radioactivity of chromatographically separated substances is registered by a detector from which the pulses are transferred to an electronic counter. The use of a frequency meter as a registering device has a number of advantages in comparison with the devices used previously, *viz.*, it gives discreteness to the information obtained, direct digital registration, and the possibility of using the digital apparatus; the frequency meter sends a pulse "start printing".

A radiochromatographic device with the automatic recording of the analysis data by a printer is described in ref. 3.

The automatic recording of information stored in the frequency meter does not necessarily save an experimentalist from time-consuming work connected with data processing, as when computer processing is used, the information obtained must be presented in a form acceptable for the input device of the computer.

Fig. 1 shows a block diagram of a radiochromatograph in which teletype is used as the read-out device enabling us to make the information available on standard 17.5 mm punched tape as well as in the form of digital printing.

Each cell of the frequency meter counting decades is connected with a punching unit (teletype) through a system of inquest and control. This system consists of a

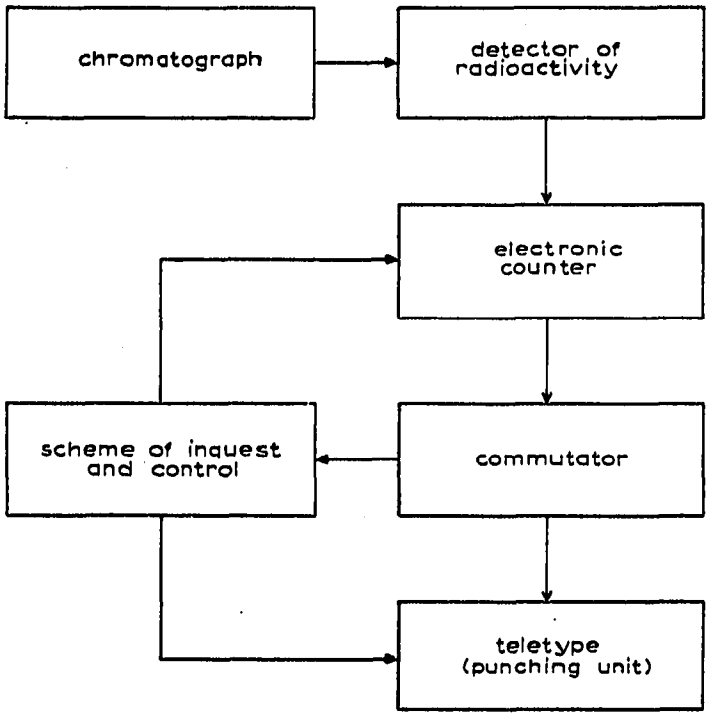

Fig. 1. Block diagram of a radiochromatograph in which teletype is used.

commutator, which is kinematically connected with the teletype and which probes each decade of the frequency meter, and a control system of the commutator for starting up the next cycle. Counting cells of all the frequency meter decades are connected with the commutator clamps. The commutator is made of a flat fixed ring, divided into $(n+1)$ equal parts, where n is the number of decades. Each of the first n parts has eight clamps used in the following way: the first clamp is for the starting signal of the teletype; the second for a synchronous pulse; the following four clamps are for passing through information from the frequency meter; the last two for the formation of the stop signal. All the clamps of the first n parts are fixed on the flat face on the side of the ring and are sensed by the main moving contact connected with the teletype shaft by a gear with a reduction coefficient of $1/(n+1)$.

The clamps for starting the investigation, for resetting of the frequency meter after punching and for starting a new cycle are fixed to the inner side of the ring and are sensed by an additional earthed moving contact. When the commutator is in operation the two moving contacts are synchronously probing either the clamps of the first n parts of the ring (the main contact) or the clamps of the last $(n+1)$-th part (the earthed contact) depending on the contact locations.

At the end of each counting cycle the electronic counting frequency meter produces a signal "print begins". This signal fires a thyratron T_1 (Fig. 2), at that moment the relay R1 is triggered and allows printing. When the contacts R_{K_2} are switched off, the current flows through the tube T_3. The teletype electromagnetic circuit is closed and the armature is activated. When the commutator earthed contact approaches the clamp "A" the relay R2 is triggered, R_{K_2} contacts close and the

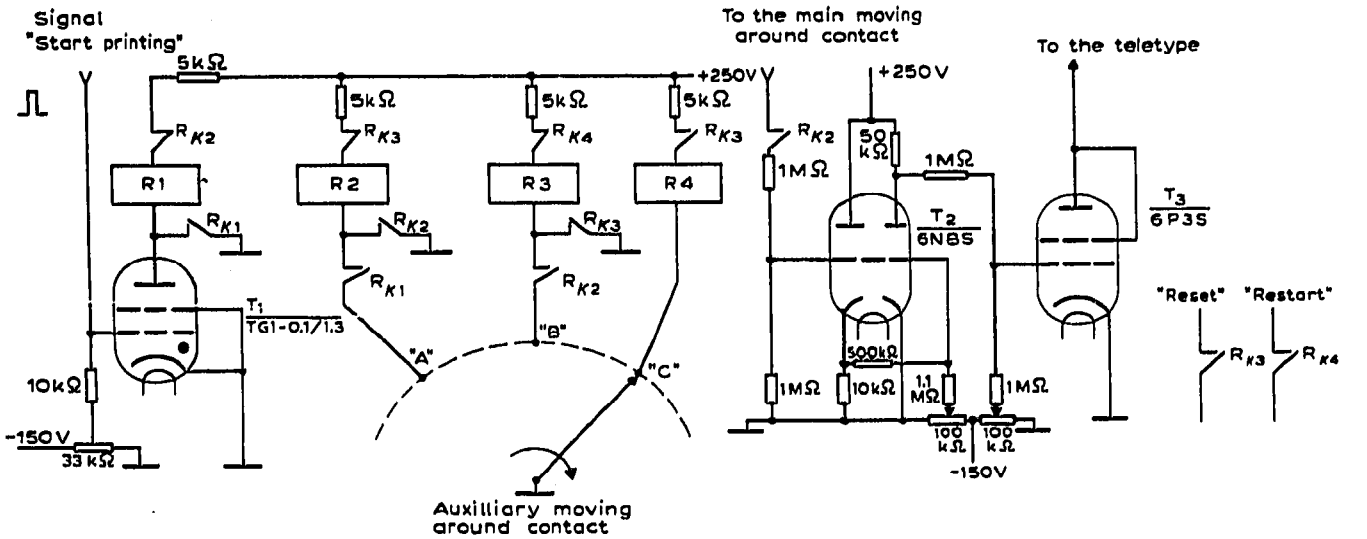

Fig. 2.

information from the main moving contact may be transferred to the tube T_2 grid, *i.e.* to the teletype electromagnet.

Voltage of +60V is applied to the first clamps of all n parts of the commutator. They are the starting clamps: when the positive signal is delivered to the input of tube T_2 the current in tube T_3 decreases and a currentless starting pulse is delivered to the teletype input.

The second clamps are freed, the voltage is not delivered to the tube T_2 input and T_3 is left in the current state. This is a current synchropulse (where current always flows).

The information from the frequency meter decades is delivered to clamps 3, 4, 5 and 6. This information is converted in such a way, that "zero" on the cell corresponds to +60V on the clamp and "unity" to zero voltage. In the first case the current does not flow through the tube T_3 (a currentless pulse) and in the second case the current does flow. The electromagnet having received the successive code of current and currentless pulses, the teletype punches and types. Each code group consists of seven pulses: "start", five pulses carrying information and "stop". Clamps 7 and 8 are vacant, that is similar to the delivery of the stop pulse.

The first clamp of the next section of the commutator then follows and the cycle is repeated; the relay of the information and the teletype punching from the second decade takes place etc.

When the earthed contact approaches "B" clamp, R3 relay operates, R2 relay switches off and simultaneously R_{K3} group of contacts performs "resetting". The tube T_3 returns to the current state. When the earthed contact approaches the clamp "C", R4 relay is triggered and a new counting cycle begins on the counting frequency meter.

The use of such a commutator instead of a selector[4] simplifies the control circuit and improves the system stability.

The punched tape obtained is put into the computer for processing of the experimental data.

When analysis is completed, successive discrete values $\{A_K\}$ are obtained.

The quantity A_K characterizes the radioactivity of the substance passing through the detector at the time t_K. The index "K" = 1, 2, 3, ..., N is determined by the expression

$$K = t_K/(\tau_1 + \tau_2) \qquad (1)$$

where τ_1 is the time of counting; τ_2 is the time of information delivery from the counting cells; it is clear that the sum $(\tau_1 + \tau_2)$ is the duration of one cycle.

To determine the relative and absolute activities of each chromatographically separated component when a large number of identical analyses are carried out the method called a "flexible calibrating net" has been suggested[5].

This method is as follows. A calibration experiment is carried out with a non-radioactive mixture of all the possible components which can be determined under certain chromatographic conditions. At the same time the beginning and the end of the component elution are determined. Using expression (1) and the times of elution, the calibrating net of the boundaries studied is thus constructed. During processing of the main experimental data the preliminary calibrating net is corrected. The peak boundaries, in comparison with the calibration ones, are corrected, over different algorithms. As a result the boundary calibrating net is transformed to the corrected boundary net. The sequence of quantities $\{A_K\}$ is divided by this net into the peak areas and background regions. It should be noted that the broadening of peak boundaries due to the background does not affect the peak area, because during the subsequent processing the correction for background is provided.

The calculations of the absolute and relative activity of separated components are made by the formulae:

(1) Determination of the absolute activity σ_j

$$\sigma_j = \frac{1}{\eta}\left\{\frac{B_j}{1 - B_j\tau} - \Phi\left[n + \frac{\tau_2}{\tau_1}(n-1)\right]\right\}$$

where

$$B_j = \sum_{C_{jl}}^{C_{jr}} A_K + \frac{\tau_2}{2\tau_1}\sum_{C_{jl}}^{C_{jr}-1}(A_K + A_{K+1})$$

Φ is the counter background; η the efficiency of detection; τ the counter dead time; τ_1 the duration of each cycle of counting; τ_2 the duration of registration; C_{jl} is the peak left hand side boundary; C_{jr} is the peak right hand side boundary; n is the number of readings of A_K in the peak equal to $C_{jr} - C_{jl}$.

If a flow counter of internal volume V is used as the radioactivity detector and when the total gas flow rate through the counter is v, the calculated absolute activity has to be corrected by the factor v/V.

(2) Determination of relative activity θ_j

$$\theta_j = \frac{\sigma_j}{\Sigma\sigma_j}\,100\%$$

Experimental studies of chemical effects of nuclear transformations[6] and studies of the effect of nuclear radiation on isotopic exchange[7] have been made by means of the technique described. Hydrogen (tritium), alkanes and olefines from C_1 to C_5 were separated chromatographically and determined radiometrically.

TABLE I

j	*Component*	*Boundary*	
		Left $C°_{jl}$	*Right* $C°_{jr}$
1	H_2	145*	166*
2	CH_4	166*	218*
3	C_2H_6	218*	265*
4	C_2H_4	265*	319
5	C_3H_8	319	426
6	C_3H_6	570	680
7	*iso*-C_4H_{10}	750	838*
8	*n*-C_4H_{10}	838*	902
9	C_2H_2	1302	1500
10	*iso*-C_4H_8	1630	1920*
11	*n*-C_4H_8	1920*	2180
12	C_5H_{12}	2500	2880

TABLE II

j	*Component*	*Boundary*	
		Left C_{jl}	*Right* C_{jr}
1	H_2	138	178
2	CH_4	178	208
3	C_2H_6	208	260
4	C_2H_4	260	319
5	C_3H_8	319	426
6	C_3H_6	570	680
7	*iso*-C_4H_{10}	750	816
8	*n*-C_4H_{10}	816	902
9	C_2H_2	1302	1500
10	*iso*-C_4H_8	1630	1880
11	*n*-C_4H_8	1880	2180
12	C_5H_{12}	2500	2880

TABLE III

j	*Component*	*Activity*	
		Absolute σ_j *(dis)*	*Relative* θ_j *(%)*
1	H_2	447 884 ± 684	96.016
2	CH_4	4 299 ± 65	0.921
3	C_2H_6	9 838 ± 99	2.109
4	C_2H_4	186 ± 14	0.039
5	C_3H_8	1 945 ± 44	0.416
6	C_3H_6	0	0.000
7	*iso*-C_4H_{10}	190 ± 14	0.041
8	*n*-C_4H_{10}	1 601 ± 40	0.343
9	C_2H_2	0	0.000
10	*iso*-C_4H_8	0	0.000
11	*n*-C_4H_8	401 ± 20	0.085
12	C_5H_{12}	121 ± 11	0.025

The standard calibrating net of boundaries was determined from the routine experiment under the following conditions: the liquid phase was liquid paraffin, the solid support was diatomite from Zikeev quarry (T3K), granule size 0.25–0.5 mm; the column length was 8 m, the carrier gas was helium; the pressure at the inlet was 1.4 atm; the rate of the gas flux 60 cm^3/min; the column temperature was (100 ± 0.1) °C; the time taken for counting was 1.00 sec; the time of registration was 1.07 sec[3,5].

In the calibrating net of boundaries (Table I) the index * shows the boundaries corrected during the fundamental experiments. The other boundaries are considered to be constant.

Let us consider an example: an experimental study of the nuclear radiation effect on isotopic exchange in the system $C_2H_6 + T_2$ in the gaseous phase[7].

A quartz ampoule with a volume of 10 cm^3 was filled to a pressure of 300 mm Hg with the gas mixture C_2H_6(C_2H_6–98%, T_2–2%) and irradiated by the mixed radiation flux of the reactor (the neutron dose was $2.7 \cdot 10^{17}$ nvt).

The mixture of products formed in the cell as a result of isotopic exchange and radiolysis due to radiation was put into a radiochromatography apparatus and analysed. The experimental data were automatically recorded and then processed by a computer according to the technique described above.

As a result of correcting the boundaries over the corresponding ranges a net of corrected peak boundaries was obtained (Table II).

When radiochromatography was carried out under the above conditions, we obtained three thousand numbers characterizing the change of the recorded activity in time. Arrangements of numbers in accordance with Table II over peak and background regions and the following calculation of the absolute and relative activities gave some information about each separated component (see Table III, where the results of processing of the data obtained in the example considered are given).

In this paper the results of automation of a chromatographic separation of radioactive substances are given. The radiochromatograph is described as well as the device for information delivery to the punched tape. The computer processing of the data is shown for an actual example—the experimental study of the effect of nuclear radiation on isotopic exchange in the gaseous phase.

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