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A CHEMICAL AMPLIFIER (COBALTOCOBALTIC OXIDE/SODIUM ALCOHOLATE) WITH FLAME IONIZATION DETECTION

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SUMMARY

A chemical amplifier in combination with a gas chromatograph is proposed, in which the combustion of substances over Co_3O_4 and the interaction of carbon dioxide and water with the alcoholates of alkali metals are used. It is shown that a chemical amplifier based on this system of reactions can operate in the low concentration range.

INTRODUCTION

In micro-analytical techniques "amplification reactions" can be used successfully[1]. Amplification reactions can be defined as consecutive conjugated reactions proceeding with an increase in the number of moles of the reacting substances. MARTIN, SCOTT AND WILKINS[2] conceived the brilliant idea of using the chemical amplification method in combination with gas chromatography (GC). Organic substances separated on a chromatographic column are oxidized. In order to increase the amount of carbon dioxide, the following system of reactions is subsequently used:

$$CO_2 \xrightarrow[970°]{C} 2CO \xrightarrow[670°]{CuO} 2CO_2 \xrightarrow[970°]{C} 4CO \xrightarrow[670°]{CuO} 4CO_2$$

The amount of carbon dioxide produced increases in geometric progression from the number of units of CO_2 reduction and CO oxidation. The amplification factor of this system of reactions is 2. A katharometer has been used as a detector[2].

The chemical amplification method in combination with GC can be expected to be useful in the analysis of micro-amounts of substances when the use of accumulation or concentration is not feasible.

The objects of the present study were as follows:

(1) To choose a reaction system that permits higher amplification factors to be obtained with a smaller number of units than in the copper oxide/carbon amplifier[2].

(2) To develop the design of a chemical amplifier operated at moderate temperatures.

(3) To evaluate the ability of the chemical amplifier to work in the low concentration range using flame ionization detection rather than katharometer detection, as reaction GC techniques are in some instances inapplicable to very low concentrations of substances owing to irreversible adsorption or incomplete conversion.

CHOICE OF CHEMICAL REACTION SYSTEMS FOR CHEMICAL AMPLIFIERS

Chemical reactions that can be used in chemical amplifiers can be subdivided into three groups, namely: (1) reactions proceeding with an increase in the number of molecules; (2) reactions or systems of reactions converting the products of the first type of reactions into the original compounds; and (3) ancillary reactions at the inlet of the chemical amplifier converting the substances separated on the chromatographic column into the substances used in the amplifier; and ancillary reactions at the outlet of the chemical amplifier converting the substances used in the chemical amplifier into readily detectable substances.

Among the reactions of the first type, the following should be noted: reactions of disintegration of large molecules (combustion of organic substances, thermal destruction of compounds, decomposition of complexes, crystal hydrates, or other compounds containing similar fragments). The products of the first type of reaction can be water, carbon dioxide, halogenated hydrocarbons or oxygenated compounds of elements of the original substances.

We have used combustion as one of the stages of chemical amplification reactions. For combustion in an inert atmosphere in a flow-through system, it is particularly advisable to use Co_3O_4 rather than copper oxide[3,4].

As reactions of the second type, we have studied the reactions of some organometallic compounds with the possible products of the first type of reactions. The use of organometallic compounds in chemical amplifiers has been suggested in the literature[2]. We have studied the reactions of alkyl magnesium bromides with water, ammonia, hydrogen sulphide, hydrogen chloride and other compounds containing active hydrogen, with the formation of hydrocarbons. In using low concentrations (0.01–0.001 %), however, it is difficult to obtain satisfactory results with organomagnesium compounds because of significant adsorption of substances on magnesium-hydroxide. Organoaluminium compounds (trialkylaluminium, triphenylaluminium) have been found to be suitable for use at low concentrations of water, ammonia, hydrogen sulphide and hydrogen chloride. Their reactivities, however, are too high for routine application in analytical practice.

For the present investigations, we chose to use the alcoholates of alkali metals. These compounds interact actively with compounds containing active hydrogen, with liberation of alcohol:

$$RONa + H_2O \rightarrow ROH + NaOH$$

The reactions of alcoholates have been reviewed in the literature[5].

The application of any amplifier is restricted by amplification of the background. In a chemical amplifier, the amplification limit is determined both by the increase of noise and by the spreading of the initial zone when it passes through the system of amplifier units. The increase of noise may be the result of several factors: the volatility of the reagents used in the chemical amplifier, impurities present in the carrier gas, and decomposition and dissociation of reagents.

It has been stated[6] that the thermal stability of the alcoholates of alkali metals decreases with an increase in the size of the hydrocarbon radical. Hence, while the amplification factor also increases with an increase in the length of the hydrocarbon chain, it did not seem advantageous to use alcoholates with a large number of carbon atoms. The best results were obtained with sodium *n*-butylate.

EXPERIMENTAL

One unit of the chemical amplifier comprises a combustion (cobaltocobaltic oxide) oven and a conversion (sodium butylate) column. Both the oven and the column containing sodium butylate were U-shaped tubes of quartz and glass, respectively, 8 cm long. The inner diameter of the quartz tube was 4 mm and that of the glass tube 3 mm. Co_3O_4 was used as the oxidizing agent in an amount of 1 g. The length of the oxidizer bed was 3–4 cm and the temperature of the combustion oven was 550°. The Co_3O_4 was prepared by heating cobalt oxalate at 500° for 20 h. The finely pulverized Co_3O_4 was aggregated into pellets 0.5–0.25 mm in diameter in a manner similar to that for the preparation of sorbent from graphitized carbon black[7]. The space between the bed of oxidizing agent and the bed of sodium butylate was filled with Celite. The amount of sodium butylate used was 0.06–0.08 g. The helium carrier gas was dried over molecular sieve 5A and phosphorus pentoxide. The chromatographic column was a stainless-steel tube, 3 m long and packed with Polysorb 1 (Olajn, U.S.S.R.) (a sorbent of the Porapak Q type), the diameter of the particles being 0.5–0.25 mm. The chromatograph was a Tsvett-3 instrument equipped with a flame ionization detector. The chemical amplifier was located in the thermostat behind the chromatographic column (Fig. 1). Sodium butylate was synthesized[8] by dissolving metallic sodium in absolute butanol with subsequent removal of the excess of butanol under vacuum at 200° for several hours.

For gas samples that contained significant amounts of oxygen, 0.5 g of metallic copper was placed in the combustion oven so as to absorb the oxygen of the sample.

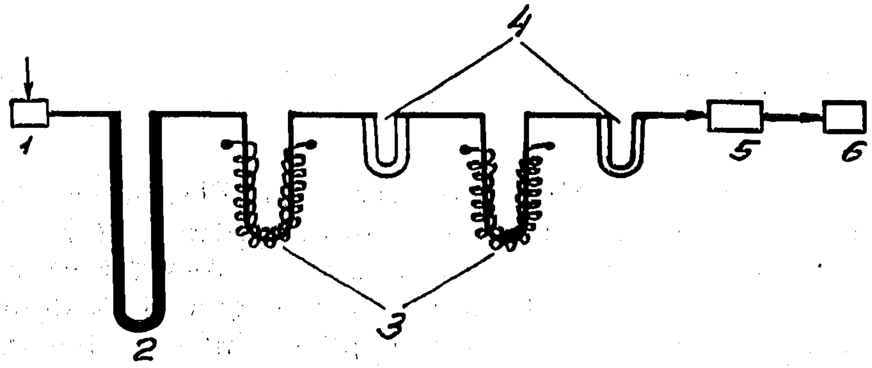


Fig. 1. Two-unit chemical amplifier. 1 = Sample injector; 2 = Polysorb-1 chromatographic column; 3 = combustion oven; 4 = tube, containing sodium butylate; 5 = flame ionization detector; 6 = recorder.

RESULTS AND DISCUSSION

We found that sodium butyrate forms volatile products not only with water but also with oxygen and carbon dioxide. As shown by GC and mass spectrometry, the volatile product of the interaction between sodium butylate and carbon dioxide is butanol.

The possible mechanism of the reaction is as follows. Sodium butylate contains sodium hydroxide as an impurity. Carbon dioxide interacts with the sodium hydroxide and liberates water, which subsequently hydrolyzes the sodium butylate with the formation of butanol:

$$CO_2 + 2\,NaOH \rightarrow Na_2CO_3 + H_2O$$

$$H_2O + C_4H_9ONa \rightarrow C_4H_9OH + NaOH$$

To confirm the absence of irreversible adsorption of water by sodium hydroxide, a column containing sodium hydroxide (0.4 g) was prepared. The water was eluted from the column 1 min later at a temperature above 100° in the form of a rather sharp peak.

Fig. 2 presents a chromatogram of the mixture of substances after passing it through one unit of the chemical amplifier. It should be noted that there are two peaks corresponding to one substance, a sharp peak that is produced by the interaction between carbon dioxide and the alcoholate, and a diffuse peak that is produced by the interaction of water with the alcoholate.

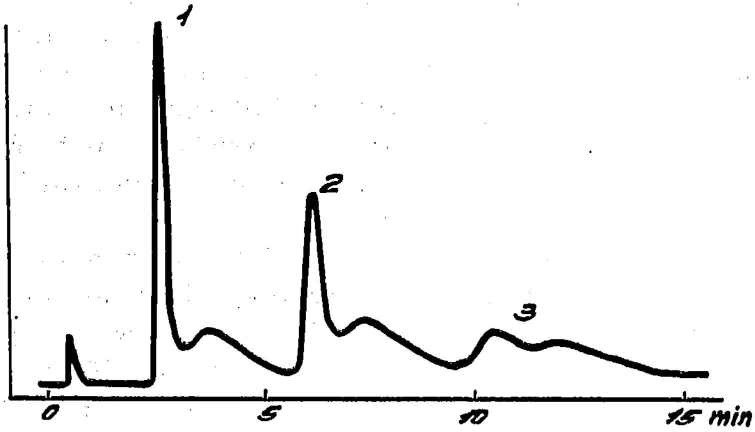


Fig. 2. Chromatogram of the mixture of acetone (1), methyl ethyl ketone (2) and *n*-butanol (3) after passage through one unit of the amplifier. The sharp peaks correspond to carbon dioxide and the diffuse peaks to water.

The total stoichiometric amplification factor for H_2O and CO_2 when the Co_3O_4/sodium butylate system is used is equal to 9. The amplification factor for CO_2 is equal to 4. As the water peak was rather diffuse, in further work the water was removed by placing a small amount of molecular sieve 5A (0.05 g) in the sodium butylate column, and all studies were made with the CO_2 peak. Our experiments showed that there is no significant adsorption of carbon dioxide on the molecular sieve in this case. A study was made of the effect of alcoholate temperature on the completeness of the reaction. As a model substance, *n*-butane at a concentration of

0.003 % (in nitrogen) was used. Fig. 3 shows the dependence on temperature of the peak area formed after the butane sample (1 ml) had passed through one unit of the amplifier. It can be seen that the optimum temperature is 150–160°.

Fig. 4 shows the effect of the carrier gas flow-rate on the peak height. The peak height strongly depends on the carrier gas flow-rate. In the subsequent experiments, a flow-rate of helium carrier gas of 1 ml/sec was used.

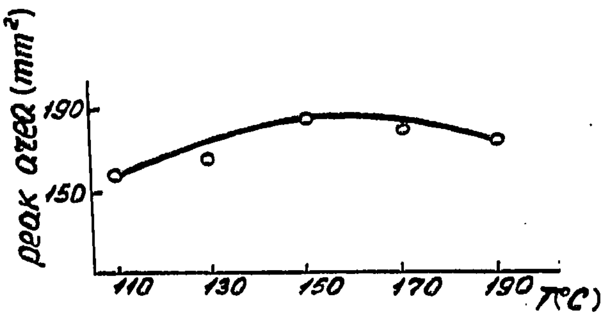


Fig. 3. Dependence of *n*-butane peak area on temperature of sodium butylate for one unit of the chemical amplifier. Sample size, 1 ml; concentration, 0.003% in nitrogen.

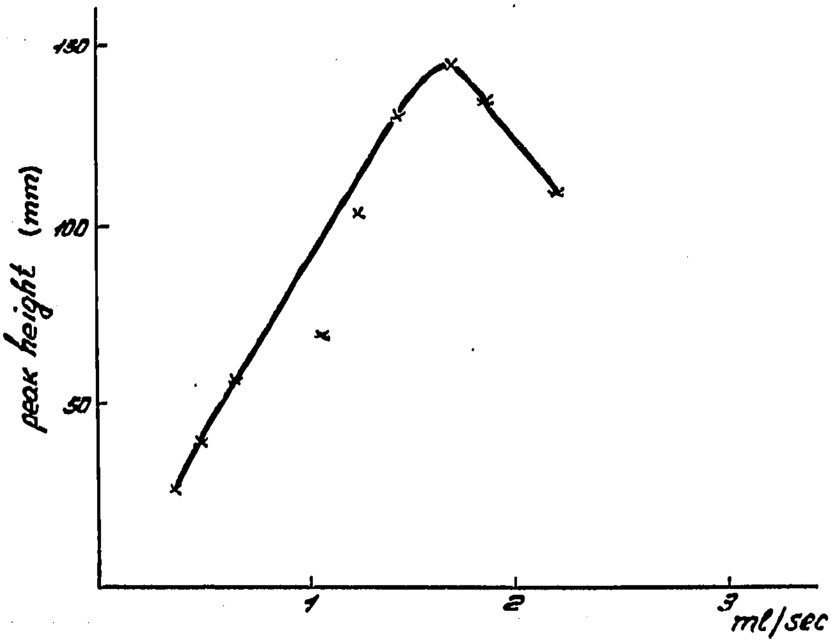


Fig. 4. Dependence of *n*-butane peak height on helium carrier gas flow-rate. Sample size and concentration as in Fig. 3.

The amplification given by one unit of the amplifier was also investigated. To ascertain this effect, as well as the effect of sample size on amplification, a graph was constructed to show the dependence of response on the amount of the substance (*n*-butane of a concentration of 10^{-2} %) after having passed through one amplifier unit and flowing without amplification (Fig. 5). Theoretically, the amplification factor should be equal to 4. From Table I, it follows that the amplification factor depends to a certain extent on the sample size. Peak areas after amplification have been re-calculated, taking into account the different sensitivities of the flame ionization detector towards *n*-butane and *n*-butanol. For the recalculation, ONGKIEHONG's method[9] was used.

The unit of the chemical amplifier described above enables reproducible results to be obtained. The relative mean quadratic error as determined for 20 samples (0.5 cm^3 of 0.03 % *n*-butane) was equal to 5.6 %.

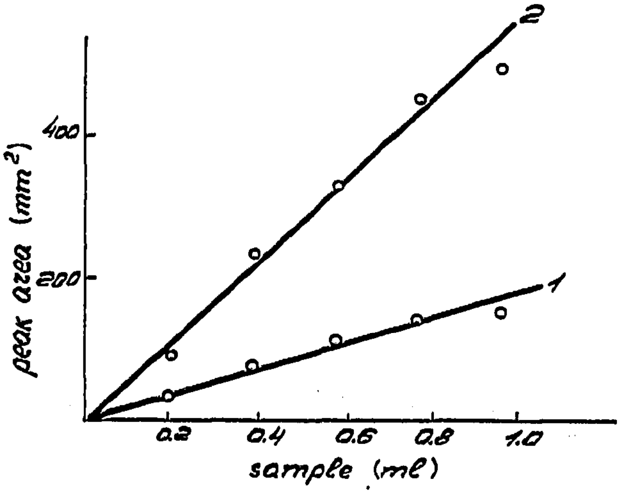


Fig. 5. Dependence of *n*-butane peak area on sample size for one unit of the amplifier. Concentration, 0.03 %.

TABLE I

DEPENDENCE OF *n*-BUTANE PEAK AREA ON SAMPLE SIZE (CONCENTRATION 0.01 %) FOR ONE UNIT OF THE CHEMICAL AMPLIFIER

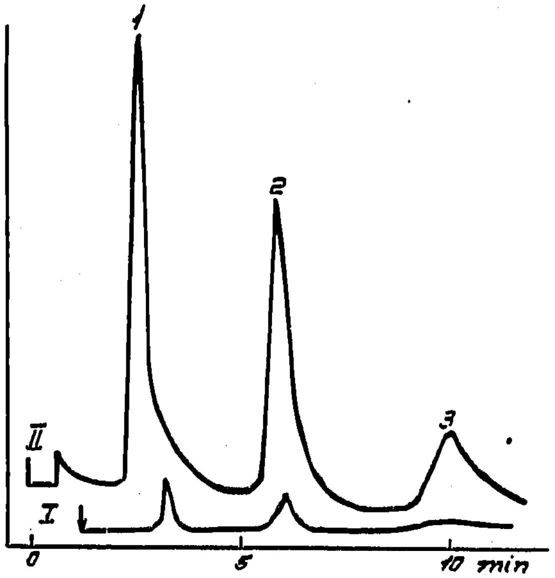
No. of experiment	*Volume of sample (ml)*	*Peak area without amplification (mm²)*	*Peak area after amplification (mm²)*	*Amplification factor*
1	0.2	43	130	3.0
2	0.4	92	350	3.8
3	0.6	132	488	3.7
4	0.8	168	675	4.0
5	1.0	179	732	4.0

From the results given for one unit of the chemical amplifier, it follows that one unit increases the amount of the substance almost theoretically. Figs. 6 and 7 show the chromatograms of a mixture of oxygenated compounds and carbon tetrachloride after these components have passed through two units of the amplifier. For comparison, chromatograms of the same mixtures without amplification are given. From these figures, the effect of amplification of micro-amounts of substances is evident. Table II presents amplification factors for a two-unit amplifier.

Theoretically, when calculated as the number of carbon atoms, the amplification factor should equal 4 for all compounds for one unit and 16 for two units.

$$1C \xrightarrow{Co_3O_4} \underbrace{1CO_2 \xrightarrow{C_4H_9ONa} 1C_4H_9OH \xrightarrow{Co_3O_4} 4CO_2}_{\text{First unit}} \underbrace{\xrightarrow{C_4H_9ONa} 4C_4H_9OH \xrightarrow{Co_3O_4} 16CO_2}_{\text{Second unit}}$$

It can be seen from Table II that the amplification factors for oxygenated compounds approach the theoretical value quite closely. The amplification factor for carbon tetrachloride is significantly higher than the theoretical value, owing to the interaction of chlorinated products from the combustion of carbon tetrachloride with sodium butylate, resulting in the liberation of additional amounts of *n*-butanol.



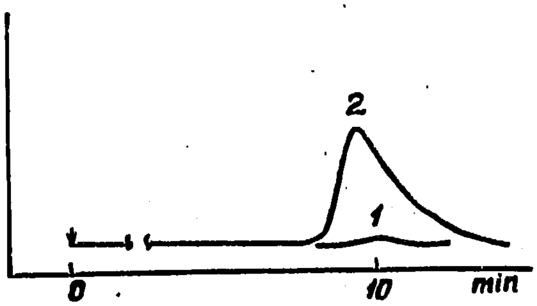


Fig. 6. Chromatogram of a mixture: 1 = acetone; 2 = methyl ethyl ketone; and 3 = butanol; I = without amplification and II = with two-unit amplification. For amounts of components, see Table II.

Fig. 7. Chromatogram of carbon tetrachloride; 1 = without amplification and 2 = with two-unit amplification. For amount of CCl_4, see Table II.

TABLE II

AMPLIFICATION FACTORS FOR TWO UNITS OF THE CHEMICAL AMPLIFIER

Component	*Sample size (mg)*	*Peak area without amplification (mm^2)*	*Peak area after amplification (mm^2)*	*Amplification factor*
Acetone	$1.7 \cdot 10^{-3}$	34	507	14.9
Methyl ethyl ketone	$1.7 \cdot 10^{-3}$	36	520	14.4
Butanol	$1.2 \cdot 10^{-3}$	12	198	16.0
Carbon tetrachloride	$3.2 \cdot 10^{-3}$	8	293	34.3
n-Butane	$6.3 \cdot 10^{-5}$	72	939	13.0

The chemical amplifier described above, when used in combination with a flame ionization detector, permits the determination of micro-amounts of compounds that cannot be detected or that are poorly detectable with this detector, such as CO,CO_2, COS,CS_2, H_2O, H_2S, HHal, NH_3,$COCl_2$, perchlorinated compounds, NOCl and S_2Cl_2.

Two units of the described chemical amplifier adequately increase the sensitivity of determination of organic and inorganic compounds. Increasing the number of units will probably give an even greater amplification.

CONCLUSION

A chemical amplifier (Co_3O_4/sodium alcoholate type) has been proposed in which an increase in the number of molecules of both water and carbon dioxide takes place. This type of amplifier is suitable for the determination of trace amounts of organic and inorganic compounds that are poorly detectable with a flame ionization detector.

The application of a chemical amplifier in GC can be considered as a development of the methods of reaction GC. As in the transition from single separation methods to repeated ones and later to chromatographic methods, the transition to multiple, repeated uses of systems of chemical reactions seems natural.

It is to be expected that in the future chemical amplifiers in combination with gas chromatographs will become established among methods for the analysis of microamounts of substances.

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