Separation of Chlorine Isotopes by Ion-exchange Chromatography

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It has been shown [1,2] that different halogen ions can be separated chromatographically in a column of an ion-exchange resin of the strong base type. It seemed, therefore, worth while to investigate the possibility of separating the chlorine isotopes in a similar way. Evidently a very long column would be necessary and so a column of, in principle, infinite length was built in the following manner.

Two glass tubes, A and B, 2.7 cm inner diameter and 150 cm long, were filled with Amberlite I R A 400 in the nitrate form. From a Mariotte bottle the eluent passing a flowmeter is led to the top of column A. Having passed this column the solution flows through a measuring device to the top of column B, and after passage of this it flows out and is discarded. By means of a system of three-way stopcocks in the tube system the eluent can be passed through the columns in the opposite order, *viz.* from the flowmeter through column B downwards to the measuring device and herefrom through column A, likewise downwards. The measuring device contains a silver-silver chloride electrode separated from a calomel electrode by a closed stopcock.

The experiment was started by pouring 15 ml of a 3.5 *M* potassium chloride solution on the top of column A. The eluent was 0.5 *M* potassium nitrate and the flow rate was 5 ml per minute corresponding to a linear velocity of 1.5 cm per minute. The adsorption band moved with about one third of this velocity. When the elution curve obtained by measuring the chloride ion concentration electrometrically showed that the whole adsorption band had passed into column B, the three-way stopcocks were turned so as to send the eluate from B to A and in this way the experiment was continued. By each passage of the elution band from one column to the other an elution curve was obtained.

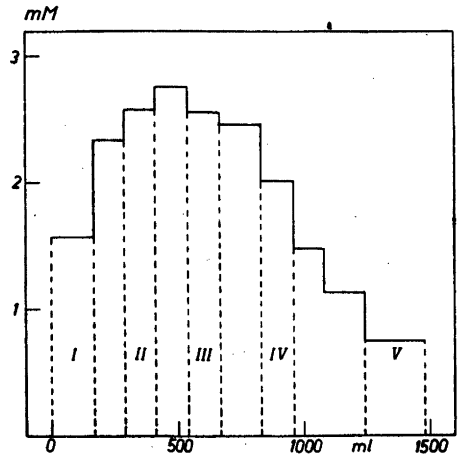

Fig. 1.

Having travelled 43 m the eluate was drawn off the apparatus, collected in fractions and titrated. This last elution curve is shown in Fig. 1 (unfortunately the first fractions were lost). The fractions indicated by roman figures were taken out for mass spectrometric analysis. The silver chloride was centrifuged down, washed and dried. It was then treated with a 25 % excess of methyl iodide in a sealed vessel for 5 hours at 100° C; this procedure resulted in a 65 % conversion. By means of a dry ice-acetone mixture the methyl chloride formed was distilled into an ampoule provided with a stopcock and a ground-glass joint intended for the connection to the mass spectrometer. This was a Metropolitan Vickers type M S 3 instrument. It has a double gas inlet system, and the measurements were carried out in the following manner. The sample was led to the ionizing chamber through one inlet

Table 1. Differences in isotopic composition obtained.

No.	R	n_R	r	n_r	Atomic fraction of ^{37}Cl	$x - 0.246$
I	0.2995±0.0019	3	0.3049±0.0012	3	0.2493±0.0024	+ 0.0033
II	0.3005±0.0005	8	0.3089±0.0006	10	0.2512±0.0009	+ 0.0052
III	0.3031±0.0007	3	0.2966±0.0003	14	0.2420±0.0007	— 0.0040
IV	0.3034±0.0005	6	0.2999±0.0006	7	0.2439±0.0009	— 0.0021
V	0.3031±0.0003	12	0.2938±0.0005	12	0.2403±0.0007	— 0.0057

and the peak heigths of masses 52 and 50 were measured alternately several times. Immediately afterwards the standard, commercial methyl chloride was led through the other inlet and measured in the same way.

The mass spectrum of methyl chloride showed peaks at masses 52, 51, 50, 49, 48 and 47 besides small peaks at 53, 38, 37, 36 and 35. Lower masses were not detectable without altering the magnetic field. The occurrence of masses 53—47 indicates the formation of ions CH_3Cl^+, CH_2Cl^+, $CHCl^+$ and CCl^+ with probably all combinations of isotopic composition. An attempt to calculate the relative amounts of the four ionic species assuming them to be independent of the isotopic composition failed. Neglecting as a first approximation ions containing ^{13}C and ^2H the peak heigth of mass 52 indicates the amount of $^{12}C^1H_3{}^{37}Cl^+$ and that of mass 50 the sum of $^{12}C^1H_3{}^{35}Cl^+$ and $^{12}C^1H^{37}Cl^+$. Measuring in units of the highest peak the total amount of mass 50 is 1, of mass 52 in the standard R and in the sample r. Then the amount of $^{12}C^1H_3{}^{35}Cl^+$ is $1-k$, k being a correction term assumed to be identical in the standard and the sample. The atomic fraction of ^{37}Cl in the standard is 0.246 and in the sample x. For the standard we get

$$\frac{R}{1-k} = \frac{0.246}{0.754}$$

from which $1 - k = 3.065\ R$. For the sample similarly

$$\frac{r}{1-k} = \frac{x}{1-x} \text{ or } x = \frac{r}{3.06\ 5R+r}$$

The results are shown in Table 1. Columns 2 and 4 contain the mean values and the mean errors calculated from the number of observations indicated in columns 3 and 5.

Although the differences are small they are significant, and in order to obtain greater effect the work is being continued.

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Note on the Wet Combustion of Ion Exchange Resins

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In connection with some studies on the exchange kinetics in ion exchange resins [1] it was necessary to determine the content of thorium, and sometimes of other elements, in a resin. Such a determination may in principle be carried out by either 1) elution of the ion from the resin, 2) dry combustion of the resin or 3) wet combustion of the resin. An analysis is then made of the eluate, ashes, or resulting solution respectively.

Elution from the resin is by far the best method when dealing with easily eluted ions in macroquantities. If, however, the ion is highly charged and consequently exhibits a high affinity for the resin and a low exchange rate, a complexing agent is almost unavoidable if complete elution in a reasonable volume of eluant is desired. In many cases the complexing agent interferes with the analysis and must be removed before it is done. As the complexing agent is frequently an organic compound it may be destroyed by either ashing or wet combustion, but if these methods are to be used it would seem to be more advantageous to apply them directly to the resin.

Dry combustion by ignition is limited to ions which do not form any volatile compounds. Even so the conversion of the ashes to a readily analyzed form may often meet with considerable difficulties.

Wet combustion, i. e. complete oxidation of organic matter by means of a liquid oxidant, is frequently employed in inorganic analysis when organic matter may interfere.

Lowen *et al.*[2] decomposed Dowex 50 with concentrated sulfuric acid in the presence of metallic selenium as catalyst. This method seems, however, to be rather time-consuming (see Table 1), and as a relatively high temperature is needed to expel the selenium it is to some extent subject to the same objections as dry ashing. The same authors carried out a combustion by treating the resin with concentrated perchloric acid for 24 hr at 50° C; a good method in principle, but much too time-consuming.