

and the peak heights 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  $\text{CH}_3\text{Cl}^+$ ,  $\text{CH}_2\text{Cl}^+$ ,  $\text{CHCl}^+$  and  $\text{CCl}^+$  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  $^{13}\text{C}$  and  $^2\text{H}$  the peak height of mass 52 indicates the amount of  $^{12}\text{C}^1\text{H}_3^{37}\text{Cl}^+$  and that of mass 50 the sum of  $^{12}\text{C}^1\text{H}_3^{35}\text{Cl}^+$  and  $^{12}\text{C}^1\text{H}^{37}\text{Cl}^+$ . 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  $^{12}\text{C}^1\text{H}_3^{35}\text{Cl}^+$  is  $1-k$ ,  $k$  being a correction term assumed to be identical in the standard and the sample. The atomic fraction of  $^{37}\text{Cl}$  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

$$\frac{r}{1-k} = \frac{x}{1-x} \text{ or } x = \frac{r}{3.065R+r}$$

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<sup>1</sup> 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.*<sup>2</sup> 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.

Table 1. Time (in minutes) necessary for complete combustion of 1 g resin samples with some different oxidants.

Resin	Particle size mm	Ionic form	Se + H <sub>2</sub> SO <sub>4</sub>	HNO <sub>3</sub> + HClO <sub>4</sub> <sup>a)</sup>	H <sub>2</sub> SO <sub>4</sub> + HNO <sub>3</sub>
Dowex 50	0.5—1.0	Na <sup>+</sup>	~200 b)	20—30	20—30
	0.6—0.8	Th <sup>4+</sup>	—	~500	20—30
Amberlite IR-100	0.5—1.0	H <sup>+</sup>	~150 b)	10—15	20—30
		Th <sup>4+</sup>	—	10—15	20—30

a) 6 + 12 ml for Dowex 50-Na<sup>+</sup> (For Th<sup>4+</sup> the acid mixture had to be renewed twice); 10 + 8 ml for Amberlite IR-100<sup>b)</sup>.

b) Including time necessary to drive off the selenium.

The most commonly used oxidizing agents which do not introduce any foreign cation are mixtures of concentrated perchloric and nitric acids and sulfuric and nitric acids, respectively. The former mixture has recently been applied to several organic compounds<sup>3,4</sup>. Thus Smith<sup>3</sup> succeeded in decomposing completely a sample of Dowex 50 (ionic form unknown) in 20 minutes. Independently of Smith, Högfeldt *et al.*<sup>5</sup> made a special study of the wet combustion of ion exchange resins of the phenol formaldehyde and polystyrene types in some different ionic forms, and finding decomposition times of the same order as Smith, see also Table 1. When using this method on Dowex 50 saturated with thorium we have found a considerable increase in the time needed for complete combustion. This may be due to the filling of the resin pores with a white precipitate which is formed during the reaction, resulting in mechanical interference with the attack of the resin. The possibility of a catalytically inhibiting effect cannot be excluded. It may be noted, however, that this inhibition was not observed with the more readily oxidized phenolformaldehyde resin, Amberlite IR-100. The latter resin has not such a dense structure as the polystyrene resin Dowex 50, a factor which may influence the oxidation rate, especially when slightly soluble precipitates are formed. The precipitate is dissolved on dilution after complete reaction. However, oxidation of Dowex 50 with concentrated sulfuric and nitric acids was found to be satisfactory even when the exchanger was saturated with thorium. A precipitate, thorium sulfate, which is poorly soluble in concentrated sulfuric acid, was formed in this case also, but it had no measurable effect on the oxidation rate.

*Experimental.* A resin sample of 1 g dried at 105° C was placed in a 30 ml Kjeldahl flask together with 20 ml conc. sulfuric acid. On heating, the resin becomes increasingly charred, and after boiling for about five minutes a black suspension is obtained. Now 10 ml conc. nitric acid are added dropwise to the boiling suspension at a rate of about 1 ml/min. The reaction is rather vigorous at the beginning, and nitric dioxide fumes are evolved. The suspension changes into a dark red solution, which gradually clears up to light yellow. Boiling is continued for five minutes after the last drop of nitric acid has been added giving a water clear solution on cooling.

A few results are shown in Table 1 in comparison with other methods.

In some cases, as for resins containing sodium and hydrogen, combustion with nitric-perchloric and sulfuric-nitric acids are of the same order of usefulness. In special cases, however, one of the methods may be preferable, *e. g.* when an ion in the exchanger forms insoluble sulfates the nitric-perchloric acid mixture is obviously the most suitable. Often, as for thorium resin, it may not be possible to judge without experiments which method is to be preferred. The nitric-perchloric and sulfuric-nitric acid methods are therefore complementary to each other in a useful manner.

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## Deacylation of N-Acetylated Amines with Alcohol and Boron Trifluoride

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On attempting to prepare 3,4-dinitro- $\alpha$ -naphthylamine<sup>1</sup> from its acetyl derivative it was found that the usual methods of deacylation were unsatisfactory, side reactions accompanying deacylation.

As stated in another investigation<sup>1</sup> 3,4-dinitro- $\alpha$ -naphthylamine is quantitatively transformed to 4-chloro-3-nitro-naphthalene diazonium chloride when heated with *hydrochloric acid*.

With *dilute sulphuric acid* it was found that acetaldehyde was formed when the acetyl compound was refluxed in a mixture

of equal amounts of ethanol and 50 % sulphuric acid which may suggest the formation of a diazonium compound that in its turn is reduced by the alcohol. The reaction with sulphuric acid is obviously similar to that with hydrochloric acid.

Attempts to split off the acetyl-group by heating the acetyl compound for a short time in *concentrated sulphuric acid* as described by Blankensma<sup>2</sup> also failed, sulphonation apparently taking place.

Roon, Verkade, and Wepster<sup>3</sup> have reported that many aromatic acetyl compounds are converted to the corresponding amine by heating with *absolute alcoholic hydrogen chloride*. However, this method was not successful in the case of 3,4-dinitroaceto- $\alpha$ -naphthalide. A product exploding very violently at ca. 150 °C was formed. It was not investigated further.

Treatment of the acetyl compound with *alcoholic aqueous sodium hydroxide* yielded chiefly products other than 3,4-dinitro- $\alpha$ -naphthylamine. The formation of ammonia indicated that the amino-group was split off.

Attempts were also made to deacylate the acetyl compound in boiling *alcohol with sodium alcoholate as a catalyst* as described by Verkade and Witjens<sup>4</sup> and this method was found to give satisfactory results.

Table 1. The results of deacylation with methanol and boron trifluoride.

Compound	Time min.	Temp. °C	M.p. * of the crude product °C	M. p. of the pure amine °C
Acetanilide	60	65	liquid ( $n_D^{20} = 1.586$ )	liquid ( $n_D^{20} = 1.586$ )
<i>o</i> -Nitroacetanilide	10	65	71—72	71—72
	35 **	65	71—72	
<i>m</i> -Nitroacetanilide	20	65	112—13	114—15
<i>p</i> -Nitroacetanilide	15	65	149—50	150—51
2,3-Dinitroacetanilide	20	65	124—25	126—27
2,6-Dimethylacetanilide	2 160	110	4—6 ( $n_D^{20} = 1.556$ )	9—11 ( $n_D^{20} = 1.561$ )
2,6-Dimethyl-N-methyl-acetanilide	2 160	110	94—95 (unchanged starting material)	liquid
4-Nitroaceto- $\alpha$ -naphthalide	25	65	192—93	196—97
2,3-Dinitroaceto- $\alpha$ -naphthalide <sup>1</sup>	60	65	(unchanged starting material)	232 (decomp.)
3,4-Dinitroaceto- $\alpha$ -naphthalide	65	65	201 (decomp.)	201 (decomp.)

\* All melting points are corrected.

\*\* Deacylation in a solution containing 0.01 g BF<sub>3</sub>/ml.