

Wet Combustion, an Alternative to Elution when Analysing Ion Exchange Resins

ERIK HÖGFELDT and PEDER KIERKEGAARD

Depts. of Inorganic and Analytical Chemistry, Royal Institute of Technology, Stockholm, Sweden

The method of wet combustion has in recent years proved to be useful when analysing organic materials for metallic constituents¹. For the analysis of ion exchange resins for small amounts of various ions, we have found wet combustion to be practicable and a valuable aid in our experiments²⁻³. As this method might be of value even in many other cases, the following results concerning the wet combustion of different ion exchange resins may be of interest.*

The ion exchange resins

Most of the experiments deal with cation exchangers, but a few experiments with an anion exchanger were also made because metals can be retained on anion exchangers as anionic complexes.

The cation exchange materials studied all contained sulfonic acid groups. They could be divided into two groups with respect to the resin structure: one consisting of phenol formaldehyde resins and the other, polystyrene resins.

As examples of the first group, Wofatit KS and Duolite C-3 were used and of the second group, Dowex 50 and Lewatit S 100. The last-mentioned was kindly placed at our disposal by Dr. H. Löffler.

The anion exchanger used was Amberlite IRA-400, which is a polystyrene divinylbenzene copolymer containing quaternary ammonium groups.

* *Note added in proof*: Unfortunately we did not recognize, before submitting the paper for publication, that Smith⁷ as well as Argersinger *et al.*⁸ used wet combustion for destroying ion exchange resins. Smith only showed the possibility of dissolving a sample of Dowex 50 of unknown composition in a mixture of nitric and perchloric acids. Argersinger *et al.* used sulfuric acid and metallic selenium as catalyst for the combustion of ion exchange resins. This method has recently been tested by Holm and Svensson⁹ who found it too time-consuming in comparison to the nitric-perchloric and nitric-sulfuric acid methods studied by them.

The experiments with the phenol formaldehyde resins

The two groups of resins behaved very differently during the wet combustion, depending upon the differences in the resin structure. The experiments with Wofatit KS and Duolite C-3 were carried out with 1 g portions of air-dried resin. Both hydrogen-, sodium- and potassium-saturated resins were used. The particle size was about 1—1.5 mm for both exchangers.

The wet combustion was carried out in tall, 200 ml Pyrex beakers in which were placed 10 ml conc. nitric acid and 8 ml conc. perchloric acid. The beaker was placed on a hot plate with a temperature of about 200—250° C. Fumes of nitrogen dioxide were immediately expelled and after about 5 minutes the reaction began with gas evolution and the solution became dark red. Within 8—10 minutes the reaction was completed and about 5 ml of a colourless or light yellow solution had been obtained. The reaction was quantitative, even stray particles adhering to the walls of the beaker were destroyed by the vapours and finally dissolved. No difference in time between the sodium and hydrogen forms could be observed.

For potassium saturated exchanger the reaction took about 15—20 minutes and a precipitate of potassium perchlorate was obtained. The formation of a precipitate seems thus to make the dissolution of the resin more difficult.

Some experiments with moist resins proved that they were nearly as easily dissolved as air-dried ones.

To study the possibility of using the method for larger amounts of resin, experiments were made with 10 g samples of air dried hydrogen-saturated Duolite C-3. For such an amount, 50 ml conc. nitric and 40 ml conc. perchloric acids proved to be suitable, and the dissolution was complete within 20 minutes.

It was also shown that a Bunsen burner was as useful as a hot plate and that the proportion, 10 ml nitric acid to 8 ml perchloric acid, could be used equally well as the proportion, 12 ml nitric acid to 6 ml perchloric acid.

As the proportions of acids mentioned above and a total volume of 18 ml for 1 g of resin gave good results no experiments were made to find out if these proportions and total amounts of acids are the most useful ones.

The experiments show that the kind of ion in the resin plays no important role (at least for the ions studied in this paper) — only if a precipitate is formed does the dissolution seem to take a longer time than usual.

In connection with this work it deserves to be mentioned that the risk of explosion seems to be very small as long as the wet combustion is carried out with a mixture of nitric and perchloric acids¹. As it might be dangerous to carry out the wet combustion only with perchloric acid it is wise as pointed out *e.g.* by Wählin¹ to have a mixture of nitric and perchloric acids in suitable proportions ready for use.

The experiments with the polystyrene resins

The particle size of the three resins was: Dowex 50 0.5—1.0 mm, Lewatit S 100 about 0.2—0.4 mm and Amberlite IRA-400 0.5—1.0 mm. All experiments using Dowex 50 and Lewatit S 100 were made with hydrogen-saturated exchanger.

For the cation exchange resins the proportions, 6 ml nitric acid to 12 ml perchloric acid for 1 g of resin proved to be suitable. For this case the proportions were more critical because too much nitric acid caused the solution to foam too vigorously, but it was not proved whether the proportions used are the most useful ones.

Experiments with both dry and moist Dowex 50 showed that it is necessary to dry moist resins in an oven at 100—110° C before the wet combustion, because water causes the solution to bump. When the resin had been properly dried, the reaction began after 15—20 minutes if the temperature on the plate was kept at about 150° C. When the reaction took place the solution foamed and by lowering the temperature the foaming was lessened so that the foam did not rise over the edge of the beaker. The reaction was finished within a few minutes, but it was, however, not quantitative. A small amount (about 1 %) of the resin, partly charred, was still undissolved. When a few drops of nitric acid were added the charred part dissolved and the residue was clear brown. After a while the particles charred again and a few more drops of nitric acid were added. This process was repeated until the residue had dissolved completely. For Lewatit S 100 this process took about 20 minutes and for Dowex 50 about 30 minutes.

For Amberlite IRA-400, 10 ml conc. nitric acid and 8 ml conc. perchloric acid for 1 g of resin proved to be suitable. The reaction was quantitative and finished within 15 minutes.

The material balance

In order to show that all ions taken up by the exchanger can be recovered after the wet combustion the following material balance studies were undertaken with silver, thorium and cadmium ions on Wofatit KS.

Silver. It has been shown by Högfeldt *et al.*⁴ as well as Bonner and Rhett⁵ that the last traces of silver are difficult to remove from some ion exchangers, and therefore for such a case wet combustion is a valuable method.

The following example is taken from an investigation of the $\text{Ag}^+ - \text{H}^+$ equilibrium on Wofatit KS at low silver concentrations using Ag^{110} as tracer². The radioactive silver was supplied from A.E.R.E. Harwell, Didcot, Berkshire, England. The experiments were carried out as follows. One g air-dried, hydrogen-saturated resin was shaken to equilibrium with 100.0 ml of a solution containing 10^{-7} C silver nitrate and sufficient nitric acid to give an ionic strength of 0.100. When equilibrium had been attained, the resin was separated from the equilibrium solution. The resin was wet combusted as described above. After dilution of the solution from the wet combustion to 10 ml in a 10 ml measuring flask the silver activities in both the equilibrium and this solution were measured in a liquid β -counter and these activities compared with the activity in the solution with which the resin was shaken to equilibrium. The results are given in Table 1.

Table 1. Material balance of Ag^+ on Wofatit KS.

Sample No.	Activity of equil. soln. cpm	Activity of resin / 10 cpm	Σ activity cpm	Introduced activity cpm	Difference cpm
1.	4 ± 1	15.1 ± 0.3	19 ± 1	20 ± 1	$-1 \pm \sqrt{2}$
2.	3 ± 1	16.9 ± 0.3	20 ± 1	20 ± 1	$\pm 0 \pm \sqrt{2}$

The term introduced activity means the activity in the 10^{-7} C silver nitrate solution with which the resin was shaken. The term Σ activity is the sum of the activity in the equilibrium solution and the activity in the resin after wet combustion. This latter activity is measured in a 10 ml volume after the wet combustion process and must therefore be divided by 10 so that it may be compared with the activity of the original 100 ml solution. As is seen from the last column the agreement is good and within the limits of experimental error.

During the wet combustion some chloride ions were formed but, because of the low silver concentration, no precipitate could be observed.

Thorium. In order to demonstrate the material balance for some more ions experiments were carried out with the thorium ion, since this ion is easily studied by radiochemical methods.

In a small column, 6×100 mm, Wofatit KS (H^+ , 0.5—1.0 mm) 5.00 ml of a 0.05 C uranyl nitrate solution in radioactive equilibrium was introduced at such a low flow rate that nearly all of the activity was retained in the resin. After washing with about 10 ml of water, which was collected together with the solution from the sorption step, the resin was transferred to a beaker and wet combusted as described above. After combustion, the solution was transferred to a 10 ml measuring flask and diluted to 10 ml with water. The activities in this solution and the wash solution were measured in a liquid β -counter thus measuring the UX_1 activity and compared with the activity in 5 ml of the original solution diluted to 10 ml. The results are given in Table 2.

Table 2. Material balance of Th^{4+} on Wofatit KS.

Sample No.	Activity of wash soln. cpm	Activity of resin cpm	Introduced activity cpm	Difference between columns 2 and 3 cpm
1.	11 ± 1	$3\ 806 \pm 33$	$3\ 799 \pm 33$	$+ 7 \pm 33 \sqrt{2}$
2.	17 ± 2	$3\ 778 \pm 33$	$3\ 799 \pm 33$	$- 21 \pm 33 \sqrt{2}$

The agreement is good and within the limits of experimental error.

Cadmium. In order to show that not only radiochemical methods are useful when analysing wet combusted resins, some material balance studies were undertaken with cadmium using polarographic methods. The column was the same as in the experiments with uranyl nitrate and the experiments were

carried out in an analogous manner. Through the column was run various amounts of a 10^{-3} C cadmium sulfate solution but no efforts were made to regulate the flow rate so that all material was retained in the resin. At the end of the process the solution was heated to dryness to expel the acids. If the solution is too acid it is impossible to run the polarograms. To the dry residue was added 0.5 C sodium chloride solution and in addition water in such proportions that 100 ml of 0.1 C sodium chloride were obtained. The wash water was also made 0.1 C in sodium chloride. The solutions were polarographed on a Radiometer Polarograph, Type: PO 3 e, and the polarograms compared with that from a standard solution run under the same experimental conditions.

For further information concerning polarography of wet combusted samples the reader is referred to the paper by Wählin¹.

The results are given in Table 3.

Table 3. Material balance of Cd^{2+} on Wofatit KS.

Introduced amount μ moles	Wash water μ moles	Resin μ moles	Σ resin + wash water μ moles	Difference μ moles	Difference %
5.00	0.00	5.00	5.00	± 0.00	0.0
5.00	0.00	5.10	5.10	+ 0.10	2.0
10.00	0.51	9.22	9.73	- 0.27	2.7
10.00	0.50	9.10	9.60	- 0.40	4.0
15.00	0.90	14.00	14.90	- 0.10	0.7
15.00	0.90	13.70	14.60	- 0.40	2.7
20.00	0.28	20.00	20.28	+ 0.28	1.4
20.00	0.28	19.60	19.88	- 0.12	0.8

The agreement is good and the experimental error seems to be what may be expected under these experimental conditions.

Suggested applications

The experiments mentioned above permit a number of suggestions for the application of wet combustion.

The experiments with silver demonstrate clearly the usefulness of the method when working with ions which can only be eluted with difficulty. Instead of obtaining a large volume we got the material in the resin concentrated in a volume of 10 ml. For all ions that are difficult to elute with or without complexing agents, wet combustion offers an attractive alternative to elution when working with small amounts (gram quantities) of resin.

It is also possible that wet combustion may be a useful alternative to elution when analysing waste waters etc. for small amounts of metals. It has been shown⁶ that it is possible to obtain the amount in the resin in a small volume by eluting from the opposite direction to the sorption step and at such a low flow rate that equilibrium is attained. This procedure, however, takes such a long time that wet combustion may successfully compete since this process is rapid if resins of the phenol formaldehyde type are used.

For radiochemists the separation of radioactive tracers on ion exchange resins followed by wet combustion permits the determination of the specific activity of the radioactive constituents.

Other possibilities surely exist and this small paper only points out the possibility of solving analytical problems not only in terms of elution but also in terms of wet combustion.

SUMMARY

It is shown that it is possible to destroy the organic constituents of an ion exchange resin by wet combustion using a mixture of conc. nitric and perchloric acids. At the end of the reaction a clear solution is usually obtained. This fact makes it possible to use wet combustion as an alternative to elution when analysing small amounts of ion exchange resins for metals. Resins of the phenol formaldehyde type are more easily dissolved than resins of the polystyrene type and are to be preferred.

Material balance studies show that wet combustion does not affect the accuracy of the analyses in the cases studied.

A number of applications are suggested and it is stressed that, when analysing for ions, which can only be eluted with difficulty, wet combustion is an attractive method compared to elution.

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