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THE DIFFERENTIAL THERMAL ANALYSIS IN THE IDENTIFICATION OF CATIONS THROUGH THE DOWEX 50W X12 RESIN

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Starting from some satisfactory preliminary studies, the possibility of identifying single cations in solution has been investigated, by means of ionic exchange with a highly acidic resin (Dowex 50W) and a subsequent study by differential thermal analysis of the same resin. A catalogue of DTA curves has been prepared with 19 ionic forms of the said resin, and it has been found that the DTA curves are sufficiently distinguishable and reproducible to suggest an eventual analytical use in more complex cases of solutions containing more than one cationic species.

To start with, given the characteristics of the ion exchange resins, it is to be expected that a resin may have its physico-chemical properties fairly unchanged in identical conditions of temperature, moisture, mesh-size, etc. since the macromolecular lattice or matrix remains unaltered anyway. However, it is also foreseeable that such properties may be a function, ultimately, of the ion or ions linked to the functional groups of the same. This at once suggests that, through the difference in the properties of the resin, it would be possible to infer the identity of the ion or ions associated to the same, since, taken as a whole, they are materials of a different composition. This may present an analytical interest, not only qualitative but also quantitative, if adequate methods are worked out.

Among the most outstanding physico-chemical properties of the ion exchange resins making possible their identification, there is their thermal stability. Several instrumental methods have been devised to follow the variations of such a property in function of the temperature, such as thermogravimetry, differential thermal analysis, etc.

Micro differential thermal analysis has been applied in this work as the main instrumental technique, since such a technique permits the elaboration of well defined DTA curves for each case under study.

In a previous work [1] we gave an account of preliminary explorations done with a series of typical ionic forms of the Dowex 50W X4 resin, in order to evaluate the degree of differentiation which can be inferred from DTA curves. The results then obtained showed that each ionic form presented some thermal characteristics so sufficiently different as to be distinguishable from the others in a reproducible manner, in the characteristic form or track as well as in the temperatures of transformation. Nevertheless, anomalies were found in the reproducibility of the lithium

and magnesium forms. This resulted in doing some work towards investigating the causes of the observed anomalies [2], several parameters being studied. One of the conclusions drawn from this study had to do with the convenience of utilizing the Dowex 50W X12 resin as virtually free from anomalies in the reproducibility of results obtained through its use.

Experimental

The resin used in the present work has been the Dowex 50W X12 resin, of sulfonated polystyrene, strongly cationic, of 100–200 mesh, with an exchange capacity of 4.9 eq/kg of dry resin in the H-form.

The method of preparation of the ionic forms of this resin consisted in passing a solution of the required cation over a bed of resin in the acid form placed in a column fitted for the treatment of about 3 g of the same. The procedure followed for the control of the exchange does not present any special peculiarity. Once the exchange had been completed, the resin was subjected to a careful washing to ensure the absence of undesirable ions which could affect the results. The washings were controlled with proper identification reactions.

The DTA apparatus used for the experiments has been a Differential Thermal Microanalyzer M–1 (Bureau de Liaison, Paris) fitted with sample-holders of the platinum cup type and platinel thermocouples. The reference material chosen was silicon carbide of 400 mesh. An atmosphere of dry air has been used, circulating at the rate of 1.5–2.5 l/hr. The heating rate was maintained within values between 12° and 18°/min. The temperature range was between room temperature and about 800°.

The salts employed for the exchange were of analytical grade. At the beginning, some irregularities were observed in the DTA curves in those cases where the level of impurities was of a higher value than that ordinarily allowed. The weight of resin used was comprised between 2 and 3 mg. Given the order of magnitude of the heat involved in the degradation reactions, it has not been necessary to work at high sensitivity , since a number of peaks would appear which would be too large for identification purposes and which would not, in general, be reproducible, which would be confusing when estimating the temperatures defining each DTA curve.

Results and discussion

The thermal behaviour of 19 different ionic forms of ion exchange resin have been studied, taking 2 to 5 samples of each form so as to place the results on a statistical basis. The results appear in Fig. 1, which shows the profiles of the DTA curves of the ionic forms examined. Moreover, the temperatures are given for the peak maximum of the estimated transformation together with the con-

fidence level of each one of them. The actual transformation temperatures are taken as the first deviation of the base line. On account of the difficulty in estimating these temperatures, because of the large number of overlapping peaks, the temperature at which the highest one appears has been taken as defining each peak, since it is most obviously detectable. In previous studies [3] it has been noticed that the temperature of a peak maximum essentially does not change for different operational conditions, in regard to the actual transformation. In fact, considering that the aim of this work is on identification this point is not of a crucial importance.

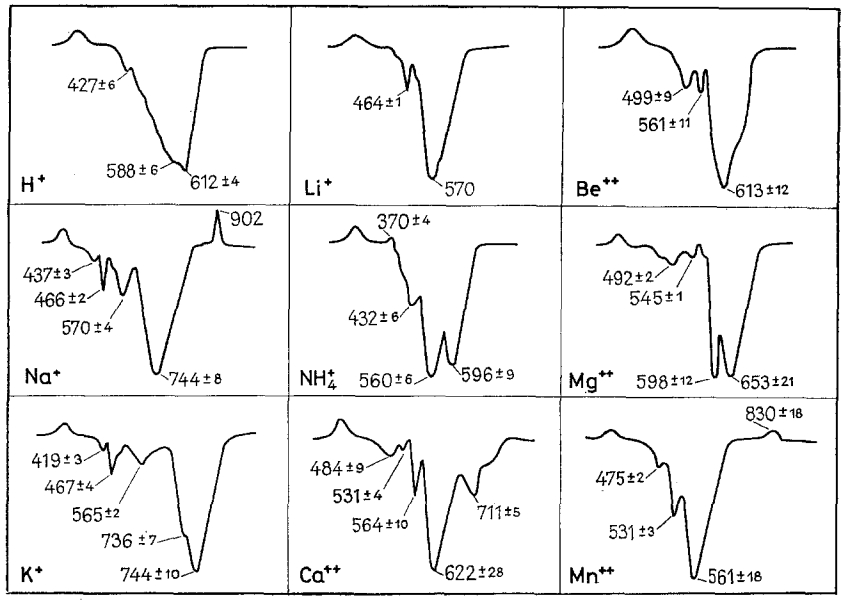
The endothermic peak of water loss is in no case taken into account as it lacks diagnostical value.

The final residue of decomposition can be an auxiliary item for identification. Table 1 lists the residual substances obtained in the thermal degradation of the different ionic forms of the resin under study.

Table 1

Cation	Residue	
	Colour	Compound
hydrogen	—	none
lithium	white	sulfate
beryllium	white	oxide
sodium	white	sulfate
ammonium	—	none
magnesium	white	oxide
potassium	white	sulfate
calcium	white	sulfate
manganese(II)	brown	oxide
iron(III)	reddish	oxide
cobalt(II)	black	oxide
nickel(II)	black	oxide
copper(II)	black	oxide
zinc	white	oxide
strontium	white	sulfate
silver	grey	metal
cadmium	white	
caesium	white	sulfate
barium	white	sulfate

In the DTA curves of the H-form a small endothermic peak appears just before the peak appearing at 427°, which is not always observed in other cases, and for this reason it has not been included in the list of the peaks which define each ionic form. The endothermic peak of the Na-form arising at 902° is due to the melting of sodium sulfate. In some of the DTA curves of the NH_4-form the two highest peaks appear superimposed in such a way that only one peak appears, together with an inflection point. The peak at 469° in the DTA curves of the Fe(III)-form



resolves to a very large number of small additional peaks for sample sizes of about 4 mg. In one of the DTA curves of the Cd(II)-form there appears a peak which overlaps the peak appearing at 606°, which was not observed in the others. The last peak of the Cs-form (720°) is of an explosive type and it originates in a swelling of the residue.

Barring a few exceptions, the temperatures of the peak maxima obtained have fallen within reasonably close limits. The confidence level (95% probability) indicates that the reproducibility of the peak maxima is good, taking into account the nature of materials handled. The peak that has been found to be least reproducible is the one at 701° for caesium, although the deviation in terms of relative confidence level is only 4.3 per cent. Normally, the most reproducible peaks make an appearance at rather low or medium temperatures (400 – 500°).

Looking at the results it can be seen that each ionic form of the Dowex 50W X12 resin presents a profile neatly characteristic in its thermal aspect. In addition, the observed peak temperatures occur in general at reproducible temperatures, so that from this data, taken as a whole, the cations associated to the matrix of the resin can be quite easily identified in cases where a single ion is involved.

In most cases the differences among the DTA curves are, in general, very marked whilst in other cases although they are significant enough should also be taken of other features. For instance, in the case of the Na- and K-forms, the aspect of the DTA curves is similar, showing, as well, three peaks which appear in common temperature zones and, although the differentiation would be possible by means of the first peak (437° and 419°, respectively) it is achieved without the least

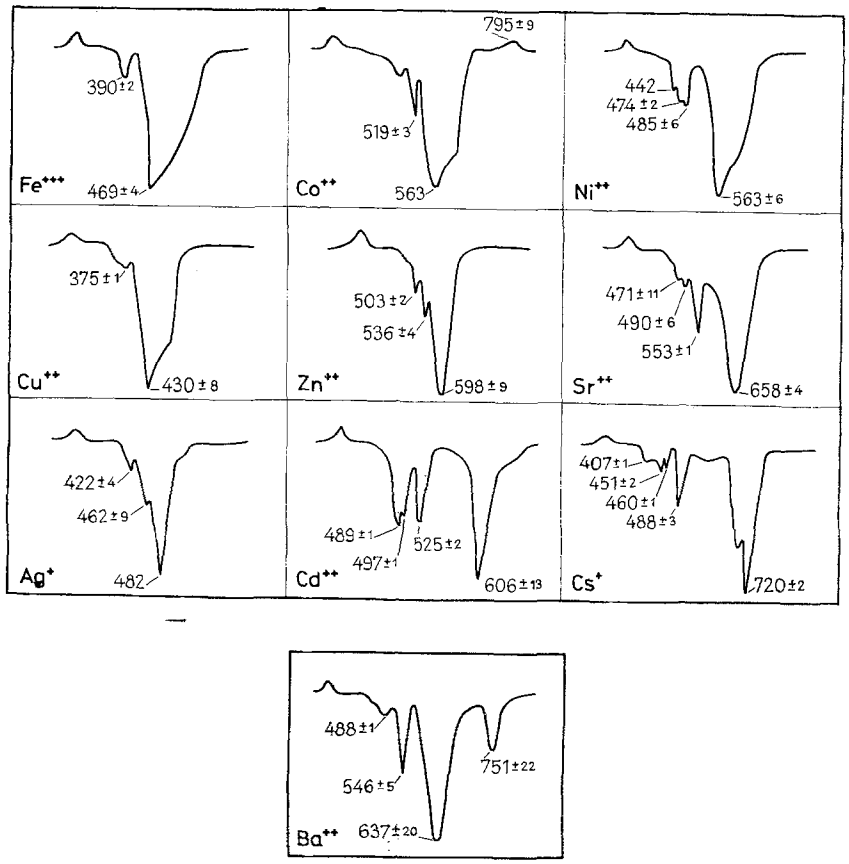


Fig. 1. DTA curves of various ionic forms of DOWEX 50W X12 exchange resin

doubt by extending the temperature range above 900°, when for the Na-form there is an additional endotherm corresponding to the melting of the sulfate. There are also similarities between the Ca- and the Ba-forms as well as in some other cases in which the elucidation is decidedly more obvious. Apart from this specific case there has not been any other case of narrow coincidence of profiles or of peak temperatures. It is to be noted that, should difficulties in identification arise from similarities in the DTA curves, it may be possible to clear up those difficulties, working in atmospheres other than air.

In those cases in which sample quantities have been used well under 1 mg, the results obtained have been irregular, which shows that the significance of the sample in this type of materials is an important factor to be taken into account, since they, as macromolecular compounds, do not have a definitely homogeneous composition. On that account, it is also important to normalize to the utmost

the procedure for the preparation of the sample, exchange, etc., so as not to introduce new factors of uncertain estimation.

Work is continuing in the field of anion-exchange resins and it can be foreseen that the general considerations which apply in the case of the cation-exchange resins do apply, as well, to them. Studies are also being made on multiple ion forms.

References

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RÉSUMÉ — Après quelques essais préliminaires ayant donné satisfaction, on a recherché la possibilité d'identifier des cations présents seuls en solution par échange ionique sur une résine fortement acide (Dowex 50W et étude ultérieure de cette même résine par ATD. On a préparé un catalogue des courbes d'ATD de 19 formes ioniques de la dite résine. Les courbes se distinguent suffisamment les unes des autres et sont assez reproductibles pour suggérer leur emploi éventuel au cas plus complexe de solutions contenant plusieurs espèces cationiques.

ZUSAMMENFASSUNG — Ausgehend von befriedigenden Vorversuchen hat man die Möglichkeit der Identifizierung von einzelnen Kationen in Lösung mit Hilfe Ionenaustausches am hochsauren Austauscherharz (Dowex 50W) und darauffolgender differentialthermoanalytischer Prüfung des Harzes untersucht. Es wurde ein Katalog der DTA Kurven von 19 ionischen Formen des erwähnten Harzes aufgestellt. Die DTA Kurven sind genügend unterschiedlich und reproduzierbar, um eine analytische Anwendung von komplizierteren Fällen mit mehr als einem Kation in der Lösung vorzunehmen.

Резюме — На основании предварительного изучения исследована возможность идентификации с помощью ДТА-анализа ионнообменной смолы сильнокислого характера (Dowex 50W). Сняты ДТА-кривые вышеуказанной смолы с 19 разными ионами и обнаружена удовлетворительная различимость и воспроизводимость. Предлагается аналитическое применение методики для более сложных случаев, когда в растворе содержится более чем один катион.