

PREPARATION AND ANALYSIS BY ION EXCHANGE TECHNIQUES OF SODIUM SALTS OF MANDELIC ACID DERIVATIVES^{1, 2}

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ABSTRACT

Ten sodium salts of mandelic acid derivatives were prepared and analyzed. Results obtained by an ion-exchange-titration method of analysis agreed with those obtained by a gravimetric procedure.

Salts of medium- to high-strength acids cannot be accurately titrated in aqueous medium. While gravimetric or other methods of determination are generally available for inorganic salts, alternate methods may not be available for salts of organic acids. Marconi (1951) has pointed out that such salts can be rapidly and conveniently titrated by employing ion-exchange techniques. Thus the cation of the salt can be exchanged for a hydrogen ion using a cation-exchange resin or the anion of the salt can be exchanged for a hydroxide ion, using an anion-exchange resin. In either case, a titratable acidic or basic solution is obtained, which has a stoichiometric relation to the original amount of the salt present.

TABLE I
Analysis of Sodium Mandelate Salts

Sodium Salt of	Salt, per cent, standard deviation		
	Anion-Exchange Titration	Cation-Exchange Titration	Gravimetric
mandelic acid	99.84±0.02	99.94±0.03	99.07±0.30
2-bromomandelic acid	99.75±0.06	99.60±0.06	98.21±0.70
3-bromomandelic acid	99.41±0.08	99.24±0.07	98.86±0.20
4-bromomandelic acid	99.83±0.05	99.12±0.16	98.78±0.34
2-chloromandelic acid	98.84±0.04	99.93±0.04	97.04±0.18
4-chloromandelic acid	99.81±0.07	99.82±0.05	99.54±0.05
2,4-dichloromandelic acid	49.86±0.04 ^a 99.21±0.06 ^b	99.82±0.03	98.46±0.40
4-ethylmandelic acid	50.45±0.05	99.63±0.07	98.76±0.42
4-methylmandelic acid	99.75±0.08	98.90±0.07	99.09±0.13
2,4-dimethylmandelic acid	99.83±0.03	99.79±0.08	99.43±0.28
2,5-dimethylmandelic acid	99.85±0.06	99.96±0.03	98.75±0.48

^aSalt filtered from solution. No evaporation to dryness.

^bSolution of salt evaporated to dryness as in other preparations.

The method of determination, then, consists essentially in passing solutions of the salts over cation- or anion-exchange resins in the hydrogen or hydroxide form, followed by titration of the effluents with standard base or acid respectively.

Ten salts of mandelic acid derivatives were prepared by the method of Ross and Morrison (1933). The purity and composition of the salts so prepared were established by passage of solutions of the salts over cation- and anion-exchange columns, after which the effluents were titrated with standard base or acid. The

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validity of the technique was checked by a gravimetric procedure involving addition of solutions containing zirconium to solutions of the mandelate salts, and ignition of the the collected mandelate precipitates to zirconium oxide for weighing. The results are tabulated in table 1.

RESULTS AND DISCUSSION

The results of the zirconium mandelate analyses point to successful preparation of mandelate salts. A maximum error of 3 per cent was observed between the analytical results and the expected result of 100 per cent for a pure compound. This is considered adequate to establish the fact that mandelate salts had been prepared, especially since the evidence is complementary to the ion exchange-titration data. Also, it should be noted that only four of the mandelic acids had been previously reported as quantitative precipitants for zirconium, namely mandelic, p-chloromandelic, p-bromomandelic, and p-methyl mandelic acids (Oesper and Klingenberg, 1949). These gave results within 1.2 per cent or less of the expected value.

The titration results were sufficiently close to the expected value to indicate that the mandelate salts had been prepared and that the ion-exchange-titration procedure is valid for mandelate salts. The data indicate that neutral salts were obtained in all cases except the 4-ethyl and 2,4-dichloromandelates. In these instances, the data indicate the formation of an acidic double salt. In the case of 2,4-dichloromandelic acid, both types of salts were obtained by variation of the technique of preparation. Note that neither the cation-exchange-titration nor the gravimetric data provide evidence for or against the formation of an acidic double salt. Conversely, the anion-exchange-titration serves as a method of detecting the presence of acidic double salts.

EXPERIMENTAL

Preparation of sodium mandelate salts

About 10–15 grams of mandelic acid were gradually added to a solution of 2.5 grams of sodium carbonate in 50 ml of distilled water. The solution was heated for a short time after which the water was evaporated in a water bath. The residue of solid was treated with 20 ml of ether and filtered. The solid was dissolved in the minimum amount of hot methanol and then an amount of acetone equal to ten times the amount of alcohol used was added. This mixture was placed in a refrigerator for at least two days. The crystals which formed were filtered, washed with ether to remove unreacted acid, and dried in vacuum at 90°C for 2 to 3 hours. In the case of 2,4-dichloromandelic acid, two methods of preparation were employed. In the first method, the crystals of salt which separated immediately upon addition of acid to the solution of sodium carbonate were filtered off and carried through the methanol-acetone purification process. These crystals, when put through the anion-exchange-titration procedure, gave results which indicated that an acid salt had formed. In the second method, procedure was the same as for all other preparations and gave a product which, when carried through the anion exchange-titration procedure, gave results that indicated that a normal salt had formed. The actual sodium salts which were prepared are listed in Table 1. Mandelic acid derivatives employed in these preparations were obtained by methods described by Perry (1955) and Johnson (1962).

Preparation and operation of the ion-exchange columns

Six ion-exchange columns of the type pictured in figure 1 were constructed. Six columns permitted simultaneous running of the cation- and anion-exchange process in triplicate. Each column consisted of a glass tube 0.5 inch in diameter and 24 inches long. Three columns were filled with 15 grams each of Amberlite IR-120 cation-exchange resin and three were filled with 15 grams each of Dowex

2 anion-exchange resin. Funnel tubes at the top were used to contain the salt solution prior to passage over the columns, and capillary tubes of about 2 mm diameter served to keep the water-solution levels higher than the resin at all times, as well as to assist control of the flow rates.

The cation-exchange resin in the columns was prepared by passage of 150 ml of 1 N hydrochloric acid over the columns. The resin was then washed with distilled water until the effluent tested neutral. The anion-exchange resin in the column was prepared by four or five alternate treatments with 1 N hydrochloric acid and then 0.5 N sodium hydroxide solutions followed by washing with distilled water until the effluent was neutral.

A blank test for acid and alkali was carried out by passing 125 ml of the distilled water used over each column at a flow rate of 4–5 ml per minute. The effluents were titrated with standard acid or base. An average blank of 0.0370 ± 0.002 milliequivalents per 125 ml of water was obtained.

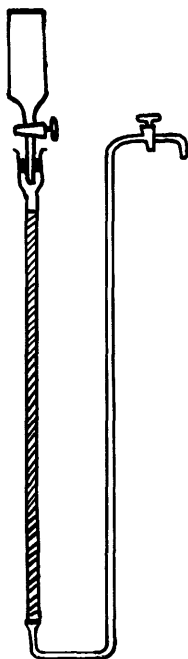


FIGURE 1. Ion exchange apparatus. Scale 1:8.

The sodium mandelate salts were prepared for analysis by dissolving accurately weighed samples of approximately 1 gram each in water and diluting to 500 ml in a volumetric flask. Twenty-five-ml aliquots were placed in the funnels at the tops of the columns. The stop cocks were opened and the flow rate adjusted to 4–5 ml per minute. As the solution passed out of the funnel and into the column, it was replaced by 25 ml increments of distilled water. Four increments were added, giving a total volume of 125 ml. The accumulated effluents of sample solution and distilled water were collected in 250 ml Erlenmeyer flasks for titration.

Titrimetric analysis of the ion-exchange effluent

The effluents from the cation-exchange resins were treated with 30.00 ml of 0.1600 N sodium hydroxide, boiled for 3 minutes, and back titrated with 0.0938

N hydrochloric acid, using phenolphthalein as indicator. The effluents from the anion-exchange columns were titrated directly with 0.0938 N hydrochloric acid, using bromothymol blue as indicator. Each sample was run in triplicate over each type column. A compilation of the results is presented in table 1.

Gravimetric analysis

Fifty ml aliquots of the solutions of mandelate salts previously prepared were acidified with 5 drops of 0.1 N hydrochloric acid. Three ml of 0.05 M zirconyl solution were added with stirring from a buret. The mixtures were then heated to 85°C and digested at this temperature for 15–20 minutes. The precipitates which formed were filtered in previously weighed Selas crucibles. The precipitates were washed with about 30 ml of hot water added in small portions with a dropper. The precipitates were then dried, ignited to the oxide, and weighed. All salts were run in triplicate. The results are given in table 1.

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