

THE LANTHANUM NITRATE TEST FOR ACETATE IN INORGANIC QUALITATIVE ANALYSIS

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Received November 28, 1940

DAMOUR¹ found that when lanthanum salts are treated with iodine and ammonia in the presence of acetic acid or acetates under suitable conditions, a dark blue precipitate or a blue solution is obtained. Though this reaction has been known for a long time, it is only during recent years that Krüger and Tschirch have adopted the reaction for the detection of the acetate ion. In a series of papers²⁻⁹ these authors have shown that the test is more delicate than any previously described for acetate, it being as sensitive as the starch test for iodine and quite as satisfactory for the detection of acetate and acetic acid in organic and inorganic material.

The test has been shown to be applicable in the presence of a large number of inorganic acid radicles.^{7,10} Nitrates, chlorides, bromides and iodides do not affect the sensitiveness of the test even when present in excess but they weaken the intensity of the blue colour. Sulphates, however, interfere in relatively small amounts, though they do not precipitate the lanthanum. Other anions such as the phosphate, fluoride, tartrate, oxalate (which precipitate the lanthanum) and the cations which are precipitated by ammonia, interfere. It has also been found that potassium iodide, or a large excess of acetate itself, tends to transform the blue colour into a yellowish brown.³ The test is very sensitive and can detect as small a quantity as 0.1 to 0.05 mg. of acetic acid, the concentration limit being 1 in 2,000 of water.^{10, 11}

Krüger and Tschirch have suggested the elimination of sulphate and phosphate⁷ with barium nitrate, the test being carried out with the filtrate. Large amounts of nitrate and chloride can be removed by making use of the fact that sodium acetate is considerably more soluble than sodium nitrate or chloride in absolute alcohol.⁸ Oxalic acid is removed by oxidation with bromine water. Separation from tartaric acid is effected by the distillation of acetic acid.⁷ It has also been suggested that distillation of the easily volatile acetic acid is serviceable for the preparation of a suitable solution for the test.⁸

In the course of the qualitative analysis of mixtures of inorganic substances including the organic radicles, acetate, oxalate and tartrate, the need for a satisfactory test for the acetate ion has been frequently felt. Several of the available tests are unsatisfactory for one reason or another. The frequently suggested test with ferric chloride is not satisfactory as pointed out by Curtman and Harris,¹² while the cacodyl oxide test cannot be recommended for general use on account of the extremely poisonous character of the product. Further, it is well known that success with the ethyl acetate test which is most commonly used, is largely dependant on personal factors. The difficulties of this test are also enhanced by the presence in the mixtures of acid radicles which evolve gases with dilute or concentrated sulphuric acid. The expedient of pouring the solution, after esterification with concentrated sulphuric acid, into water is not always satisfactory. The use of amyl alcohol^{13,14} in the place of ethyl alcohol is also unsatisfactory for the same reasons. It is apparent, therefore, that a visual test would be far superior to the olefactory ones. Tests based on crystal formation with sodium uranyl formate or cholesterol are in use in micro-chemical work but they cannot be recommended for routine analysis. Colour tests based on (a) the reduction of acetic acid to the aldehyde with magnesium and dilute hydrochloric acid¹⁵ or (b) the dry distillation of the calcium salt with calcium formate,¹⁶ and the testing of the aldehyde with sodium nitroprusside, and (c) the production of acetone by the dry distillation of calcium acetate and the testing of the vapours with alkaline *o*-nitrophenol or *o*-nitrobenzaldehyde^{17,18} are all unsuitable for mixtures of inorganic substances met with in routine analysis.

Though the lanthanum nitrate colour test has been included among tests for acetate by McAlpine and Soule¹⁹ as well as by Engelder and Dunkelberger,¹⁴ it appears that no attempt has so far been made to adapt this test for routine analysis of mixtures of inorganic substances including the acetate, oxalate and tartrate radicles. Lanthanum nitrate (Merck's "Pure") is not much more expensive than silver nitrate and the authors of this paper, therefore, felt it desirable to study the application of this reaction in routine analysis.

Experimental

Preparation of Reagents—

(1) *Lanthanum Nitrate Solution.*—5.0 g. of a sample of the "pure" salt supplied by the firm of Merck was dissolved in 100 ml. of water.

(2) *Iodine Solution.*—Krüger and Tschirch,²⁴ and Engelder and Dunkelberger (*loc. cit*) used an alcoholic solution of iodine to avoid

possible interference from potassium iodide. On the other hand, Feigl¹¹ apparently uses an aqueous solution containing potassium iodide.

The iodine solution employed in the present investigation was prepared by diluting a 0.1 N aqueous solution of iodine containing potassium iodide, prepared for volumetric analysis, with water to yield a 0.02 N solution. There was no noticeable interference in the test from the potassium iodide.

(3) *Ammonia Solution*.—The bench dilute ammonia solution (2 N) was diluted with water to yield 1.0 N solution.

Distillation of Acetic Acid from the Mixture—

The procedures recommended for the elimination of the interfering radicles by previous workers are elaborate and slow. The sodium carbonate extract which is commonly used for the identification of acid radicles is not satisfactory for while it removes most of the interfering metals, it leaves the interfering acid radicles in solution. Distillation, as suggested by Krüger and Tschirch (*loc. cit.*), of the acetic acid in the mixture with dilute sulphuric acid and absorption of the vapours in water was, therefore, considered to be the most suitable method for the preparation of the solution.

Slightly different procedures, as described below, were adopted according to the presence or absence in the mixture of sulphites and thiosulphates as shown by preliminary tests. The distillation was ordinarily carried out in a test-tube provided with a cork and a delivery tube but when the volume was large or bumping anticipated, a small distilling flask provided with a suitable adapter with an elongated tip was used. In both cases the vapours were received under a small amount of water placed in a test-tube.

(a) *In the Absence of Sulphites and Thiosulphates*.—The mixture (2–3 g.) was treated with an excess of dilute sulphuric acid (4 N) and after allowing sufficient time for any effervescence present to cease, the mixture distilled for 5–10 minutes.

(b) *In the Presence of Sulphites and Thiosulphates*.—The mixture (2–3 g.) was acidified with a large excess of dilute sulphuric acid and treated gradually with an excess of a saturated solution of potassium permanganate to oxidise the sulphur dioxide. The mixture was then distilled for 5–10 minutes as before.

Detection of Acetate—

The aqueous distillate was cooled and treated successively with 1 c.c. of lanthanum nitrate solution, a slight excess of the iodine solution and a few drops of dilute ammonia. If no blue colour developed within a minute,

the solution was gradually heated to boiling. When an acetate was present in the mixture, a dark blue colour was frequently obtained in the cold itself and without failure on gradually heating to boiling. On setting aside the boiled liquid, a deep blue gelatinous precipitate separated out in most cases when an acetate was present. If no acetate was present, only a greyish gelatinous precipitate was obtained on boiling.

Results

A large number of mixtures containing several combinations of the common acid radicles and including especially those that are likely to interfere, were examined. When no permanganate was used for the oxidation of sulphur dioxide, sulphites and thiosulphates interfered on account of the formation of the interfering sulphate ion during the test. The presence in the distillate of moderate amounts of free chlorine or bromine, oxides of nitrogen from nitrites or hydrogen sulphide from sulphides, did not interfere with the test, provided enough iodine solution was added to leave a small excess of free iodine, and was followed by sufficient dilute ammonia. In the presence of sulphites and thiosulphates in the mixture, addition of an excess of a saturated solution of potassium permanganate to the acidified mixture was found to be quite effective in preventing the liberation of sulphur dioxide. Using this modification it was found that no interference occurred with any of the common acid radicles and the results were quite satisfactory for acetate. When mixtures which did not contain the acetate radicle were examined, uniformly negative results were obtained. It was also found during this investigation that it was advisable to prescribe distillation for 5-10 minutes in all cases since in a few cases shorter periods were found to be insufficient.

Conclusion

The lanthanum nitrate test for the acetate ion has been examined for use in the routine analysis of mixtures of inorganic substances including the acetate, oxalate and tartrate radicles. A distillation method for the preparation of the test solution and a modification of this procedure in the presence of sulphites and thiosulphates are described. The results obtained are quite satisfactory and the test is recommended for general use.

The authors wish to thank Professor T. R. Seshadri for his interest in the work.

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