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ELIMINATION OF INTERFERING SUBSTANCES IN SPECTROPHOTOMETRIC DETERMINATION OF PHOSPHORUS IN FERTILIZERS

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Introduction

To obtain a commercial measure of the value of phosphorus in fertilizers, samples are heated with water and neutral or ammonia alkaline ammonium citrate solutions, or citric acid in the case of basic slag, and the phosphorus content in the extract is determined. This is done according to official methods which may differ in the various countries. With the trend towards less time consuming methods of analysis, the molybdo-vanadate spectrophotometric methods for phosphorus has attained growing interest. It has been accepted as official in the U.S.A. and is being introduced in the U.K.

However the presence of citrate ion above a certain limit interferes with the color development. Destruction of the citrate is the logical way to eliminate its interference and to make a general adaptation of the spectrophotometric method possible. This can be done by a wet-ashing procedure (1, 2, 3, 4). When applying this technique, a more detailed study was found necessary to obtain the highest possible accuracy.

Errors in General

Spectrophotometric methods are often declared unreliable owing to a variety of possible sources of error. It is however the author's experience that very often there is a lack of knowledge on how to design and carry out a spectrophotometric determination to obtain the highest possible accuracy. Further the handbook literature generally takes these matters too lightly. A general treatment of factors influencing the precision in a form adapted to practical application has been presented by the author (5), to which reference should be made.

Solutions for P_2O_5 determination

Reagent solution. Dissolve 20 g of ammonium molybdate in 400 ml of water at 50°C and 1 g of ammonium vanadate in 300 ml of water and acidify the latter with 140 ml of concentrated nitric acid sp.g. 1.40. Add slowly under agitation the molybdate solution to the acid-vanadate solution and dilute to 1000 ml.

Standard phosphate solution. Potassium dihydrogen phosphate is dried 2 h at 105°C, ground and dried another 2 h at 105°C. Dissolve 0.4793 g of the reagent in water and after the addition of a few drops of chloroform as a preservative, dilute in a volumetric flask to 1000 ml. This standard solution contains 0.25 mg of P_2O_5 per ml.

Reference solution. Measure with a piston burette 20 ml of standard phosphate solution to a volumetric flask, add 30 ml of reagent solution and dilute to 100 ml. The reference solution thus contains 5 mg of P_2O_5 (5, 6).

Note. Reference and sample solutions are prepared at the same time and allowed to stand for at least 10 minutes for complete development of the color.

Equipment

All measurements have been carried out with a Beckman B spectrophotometer using the wavelength 4200 Å and 10 mm glass cells.

Interference of the citrate ion

The interference of the color development by the citrate ion is shown in figure 1. We find that in a final colored solution containing 5 mg of P_2O_5 per 100 ml there is no interference with a content of citrate ion up to 150 mg. At higher contents the interference takes effect and is more pronounced if the citrate ion has been added as citric acid than as ammonia alkaline ammonium citrate solution, Petermann's solution. This solution has been prepared according to the official Swedish prescription (7). Taking an aliquot of 5 mg of P_2O_5 , when extracting the water and citrate soluble P_2O_5 according to ref. 7, interference will occur with all fertilizers containing less than 21 % P_2O_5 . The limit will be 27 % P_2O_5 taking instead an aliquot of 6.5 mg of P_2O_5 . In determining citrate soluble P_2O_5 interference will occur even with the high grade fertilizers. However there will be no interference in the determination of citric acid soluble P_2O_5 . This means that in most practical cases the citrate ion interferes. As all methods of elimination or compensation of the citrate ion interference are very limited except for methods of citrate destruction, only the latter will be dealt with. Supposing we take an aliquot containing 5 mg of P_2O_5 the accompanying amount of Petermann's solution depends on the percentage of P_2O_5 in the fertilizer and the kind of extract. In figure 2 the relationship between the accompanying amount of Petermann's solution in ml and the percentage of P_2O_5 is shown. One ml of Petermann's solution contains 156 mg of citrate ion and 54 mg of ammonium ion.

Destruction of citrate in dilute ternary solution

Brabson and Wilhide (3) have studied the destruction of citrate in dilute solution. We start with their procedure.

Reagents. a. Sodium chlorate solution, 20 %
b. Nitric acid - perchloric acid solution. Add 300 ml 70 % perchloric acid to 700 ml of nitric acid sp.g. 1.40

Procedure.

An aliquot of the citrate bearing extract containing 4 - 6.5 mg of P_2O_5 is transferred to a 125 ml EM-flask. Add 10 ml of the HNO_3-HClO_4 solution and 5 ml of the $NaClO_3$ solution. Warm on a medium hot plate until the solution begins to bubble, then move the flask to low heat. Shift the flask as necessary to keep the

reaction going. Finally, evaporate to HClO_4 fumes and fume for 2 minutes. It is easier to determine the end⁴ point by fuming until crystals just appear.

Let cool and add water to dissolve the crystals. Heat 10 minutes to hydrolyse non-orthophosphates. Transfer to a 100 ml volumetric flask and dilute to about 50 ml. Add 30,0 ml of reagent solution and dilute to the mark.

Experimental.

With this destruction method the citrate is eliminated, but instead acid is introduced, which influences the acidity of the final solution. The acidity interferes with the color intensity. Thus the problem has changed character.

We now apply the destruction method to a series of solutions containing 20 ml of water and varying amounts of Petermann's solution and determine the residual amount of acid. In figure 3 we find that this amount is constant if less than 2.5 ml of Petermann's solution is introduced and that the amount considerably increases if more is introduced. As more than 2.5 ml is frequently used it is necessary to destroy the ammonium to obtain a reproducible amount of acid. Such a complication has not been reported by Brabson and Wilhide (3). They have, however, used the neutral ammonium citrate solution, thus introducing less ammonia. With 2.5 ml of Petermann's solution, 135 mg of NH_4 is introduced. After citrate destruction 91 mg remains. With 3,3 ml the corresponding figures are 178 and 157 mg. Some ammonium destruction thus occurs during the citrate destruction.

Destruction of ammonium is possible, as it might be oxidized to N_2O in a mixture of hydrochloric acid, a little nitric acid and perchloric acid in dilute solution (8). Trying different variants of ammonium destruction the following was found to be best. Proceed with the citrate destruction until the solution is colorless and let it cool. At this point sufficient nitric acid remains. Dilute with 5 ml of water and add 1 ml of conc. hydrochloric acid. Continue according to the original procedure. No ammonia remains. The residue contains 25 milliequivalents of perchloric acid.

The results reported by Brabson and Wilhide (3) showed a bias of about 0.5 % caused by the acid in the residue.

Interference of mineral acids on color development.

If, during the treatment of the sample, acid is introduced, several alternative remedies are conceivable.

1. To the reference solution (index r) the normal reagent solution is used, while for the unknown solution (index x) another reagent solution is used. Its acid content together with acid in the sample should be about the same as in the reference solution.

2. The same reagent solution is used for sample as well as for reference, but to the reference solution as much acid is added as is introduced with the sample. This can be done in two ways.

a. the acidity of the reagent solution together with acid in the sample gives a normal acidity in the final colored solution.

b. normal reagent solution is used.

3. The acid in the sample is neutralized. This could be done

a. prior to or b. after addition of the reagent solution.

Experimental

In this study 20.00 ml of standard phosphate solution has been used in the sample as well as the reference solution. Using normal reagent solution and introducing no extra acid the acidity of the final colored solution is 0.61 normal.

To study alternative 1, varying additions of nitric acid were applied to the amount of standard solution and a reagent solution was added, the acid content of which would make the final solution 0.35 normal. Those samples were compared with a normal reference. From figure 4 we see that this alternative must be rejected. A relative absorbance of 0.001 means here a relative analytical error of 0.1 %.

For alternative 2 a the sample solutions were prepared in the same way as for alternative 1 and the reference by adding 26 milliequivalents of nitric acid to the standard solution and using the special reagent solution to obtain a final normality of 0.61. Figure 5 shows that this alternative is useful, if the sample introduces 10 to 35 milliequivalents of acid to the final solution. This alternative has been suggested by Brabson and Wilhide (3) and later accepted by the A.O.A.C.(9). Such a low acidity reagent solution is however stable only for about one week.

For alternative 2 b only the normal reagent solution was used. In preparing the reference 25 milliequivalents of nitric acid was added to the amount of standard solution prior to the reagent solution. The sample solution was prepared in the same way except that the amount of nitric acid was varied. Figure 6 shows that this alternative must be rejected.

We shall now study deviations from normal conditions. Three variables of the sample solution are prepared: addition of nitric acid prior to the reagent solution - branch I in figure 7, addition of sodium hydroxide prior to the reagent solution - branch II, and addition of sodium hydroxide after the reagent solution - branch III. Here we find that the sample solution must not be alkaline prior to addition of reagent solution.

To study alternative 3 a varying amounts of sodium nitrate were added to the sample solutions. Figure 8 indicates no benefit compared to omitting the neutralization, branch I in figure 7. We find, however, that neutralization gives a positive relative absorbance and omitting it a negative relative absorbance. A partial neutralization is therefore expected to give a wider useful range owing to compensation. Figure 9 shows that this is the case. Here the acidity has been increased by 0.05 normal in the sample and varying amounts of sodium nitrate added.

For alternative 3 b neutralization of the extra nitric acid was done after addition of the reagent solution, figure 10. Up to 30 milliequivalents of acid can be introduced with the sample without any influence on the absorbance. Quite the same result is obtained using perchloric acid instead of nitric acid. To study the effect of erroneous neutralization in the sample 24 milliequivalents of nitric acid were added. After addition of reagent solution it was neutralized with varying amounts of sodium hydroxide. Figure 11 shows that an excess of sodium hydroxide is harmful and that a deficiency of up to 10 milliequivalents does no harm. During neutralization the temperature of the solution is raised several degrees, and for this reason it is necessary to cool before diluting to the mark.

Of the possible alternatives 3 b is the best choice. An excess of sodium hydroxide does less harm than with 3 a. Compared with 2 a the normal and stable reagent solution is used. It is advisable to add about 5 milliequivalents less sodium hydroxide than the amount of acid introduced with the sample.

If we now return to the modified Brauson and Wilhide destruction method, we find that 9 ml of 2 normal sodium hydroxide has to be added to the sample solution before filling to the mark.

Destruction of citrate in concentrated ternary solution

In the destruction method already described, the sample must be carefully watched during fuming as it contains perchlorates and there is risk of explosion if left alone on the hot plate. It was therefore desirable to find an alternative method without any such hazards. A method described by Gehrke and Johnson (4) using a concentrated mixture of nitric acid, perchloric acid and sulfuric acid seemed to be adequate.

Ternary acid mixture. 10 parts by volume of 70 % nitric acid, 4 parts of 70 % perchloric acid and 2 parts of 96 % sulfuric acid. Add the sulfuric acid to the nitric acid and mix well before addition of the perchloric acid.

Principle. To an aliquot of citrate bearing extract containing 4 to 6.5 mg of P_2O_5 add 5 ml of the ternary acid mixture in a 100 mg EM-flask. Heat on a hot plate. First water vapor disappears. When the temperature in the solution has reached about 140°C, destruction starts. At continued heating the discoloration completely disappears.

Experimental.

After the destruction a certain amount of acid remains in the residue. For reasons already made clear, the amount of acid in the residue must be reproducible to obtain a correct color development. Following the original prescription reproducible amounts of residual acid could not be obtained.

The study has been carried with 20.00 ml of standard phosphate solution and varying amounts of Petermann's solution in the samples. 5 ml of ternary acid mixture contains 22.5 milliequivalents of sulfuric acid, 47.5 of nitric acid and 14.5 of perchloric acid. About simultaneously with the beginning of the destruction the nitric acid evaporates. As the temperature of the solution increases, the perchloric acid also evaporates. This evaporation is completed at about 200°C. The perchloric acid has a great tendency to condensate on the walls of the flask and as long as condensation takes place complete evaporation of the perchloric acid is impossible. Condensation is avoided by covering the flask with an open steel cylinder of the same height as the flask. Further the surface temperature of the hot plate was found to be essential. The best results were obtained at 240°C. A thermostat controlled hotplate is recommended. The total time for destruction and evaporation under the described conditions was 65 minutes. If at this time a slight discoloration should remain continue for a few minutes until the solution is colorless.

Let the solution cool, add 20 ml of water and heat for 10 minutes to hydrolyze non-orthophosphates.

For partial neutralization of the acid in the residue 3.7 ml of 2 normal sodium hydroxide is added after addition of the reagent solution. Cool to room temperature before diluting to the mark.

Using this modified technique more than 40 destructions were made with varying amounts of Pefermann's solution up to 4 ml and 5 mg of P_2O_5 in the aliquot. The mean of the relative absorbance against the reference was 0.000 with a mean deviation of 0.001. The destruction method thus involves no bias.

Elimination of mineral acids in determination of total P_2O_5 .

We have now seen how the citrate interference has been converted into mineral acid interference and how this has been eliminated. Also in the determination of P_2O_5 additional amounts of mineral acids will be introduced when taking the aliquot. For different kinds of material different methods of digestion are used. Each method gives a certain acidity in the extract. Knowing this, the dilution and the size of the aliquot, the additional amount of acid is easily determined. If there are more than 10 milliequivalents in the aliquot, partially neutralize to the recommendations already given.

Colored impurities

The amount of colored metal ions in extracts from phosphate rocks and products manufactured therefrom is normally so low that these ions do not influence the spectrophotometric measurement. The most common is iron. If in the extract the ratio $Fe:P_2O_5$ is less than 0.5 the interference can be neglected. If the ratio is greater the spectrophotometric method cannot be recommended for determination of P_2O_5 , nor can it be recommended if the extract contains impurities forming colored complexes with the vanado-molybdate reagent.

Acknowledgement

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Abstract

Existing methods for destruction of citrate by wet-ashing procedures are examined. More detailed procedures were found necessary to obtain reproducible amounts of mineral acid in the residue after citrate destruction. Different ways of elimination of the acid interference on color development were investigated. The best way was partial neutralization of this extra acid after addition of the vanado-molybdate reagent solution. Application for the determination of total P_2O_5 is given.

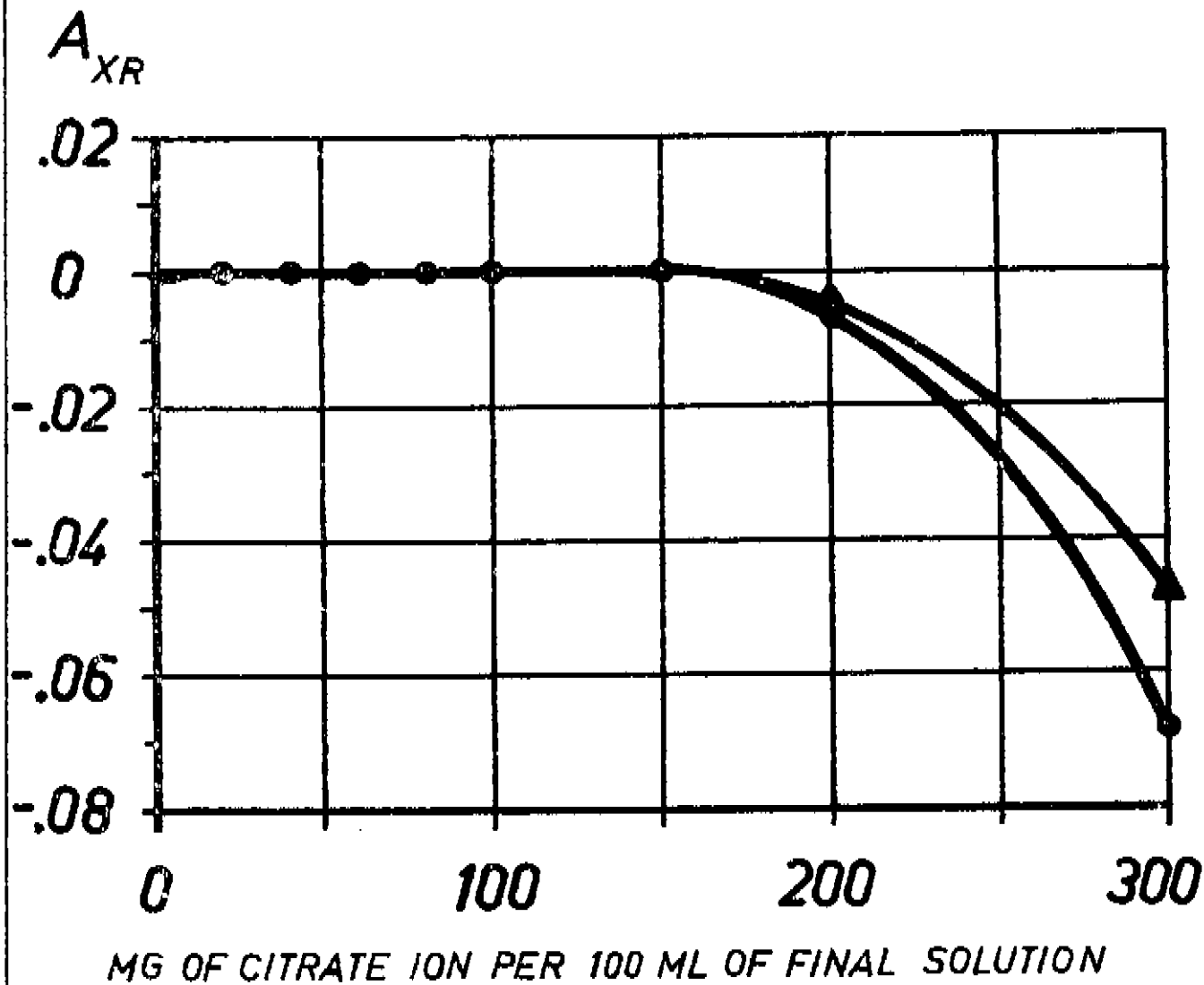
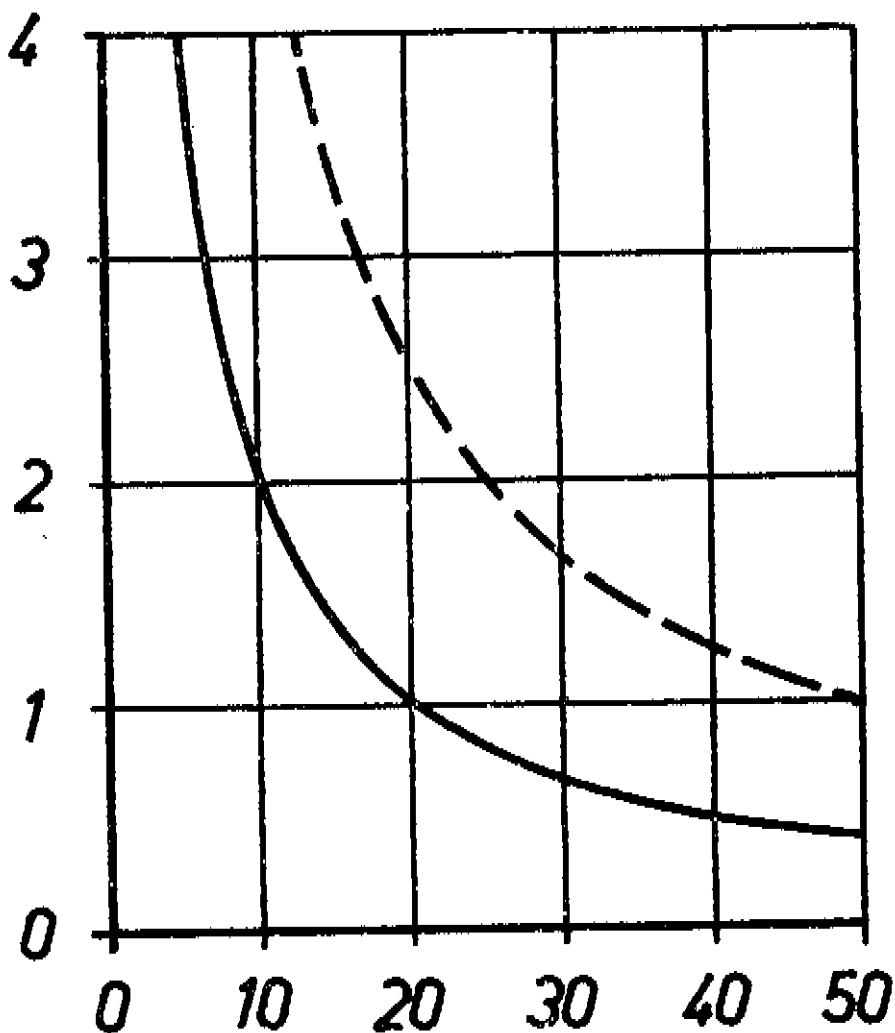


Figure 1. Interference of the citrate ion on the relative absorbance A_{XR} at 5 mg of P_2O_5 in 100 ml of final colored solution

- ▲ introduced as Petermann's solution
- introduced as citric acid

ML



% P₂O₅ IN THE SAMPLE

Figure 2. ML of Petermann's solution in an aliquot containing 5 mg of P₂O₅ in the water and citrate soluble extract (—) and in the citrate soluble extract (---) using the official Swedish method

**NORMALITY
CHANGE**

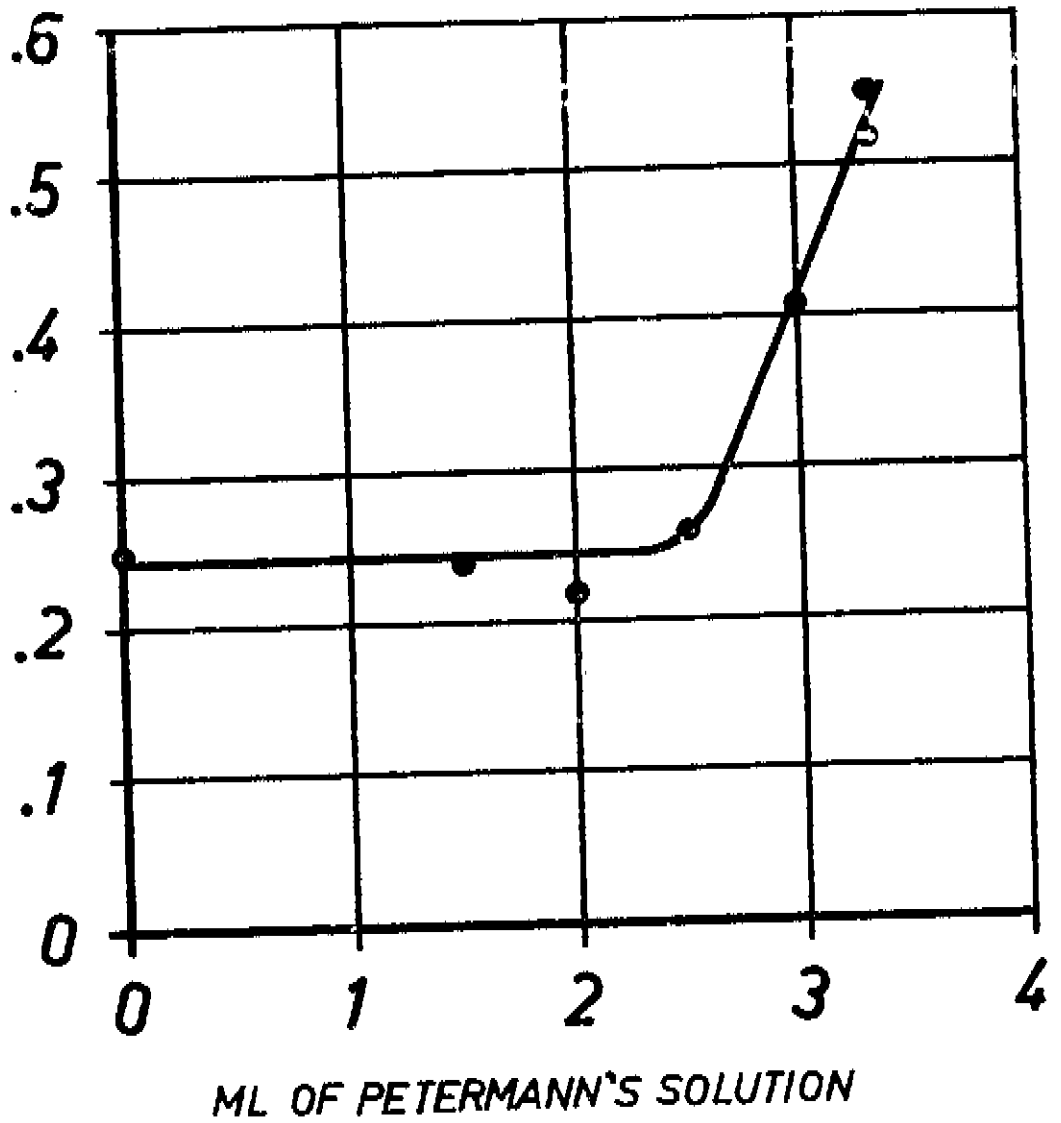


Figure 3. Additional acidity in the final colored solution introduced by citrate destruction of varying amounts of Petermann's solution in the aliquot

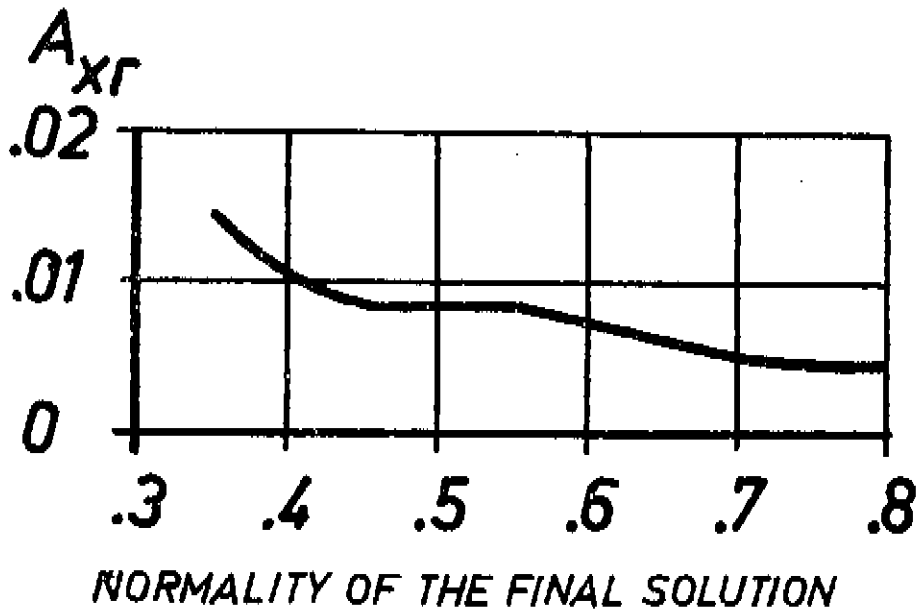


Figure 4. Remedy alternative 1

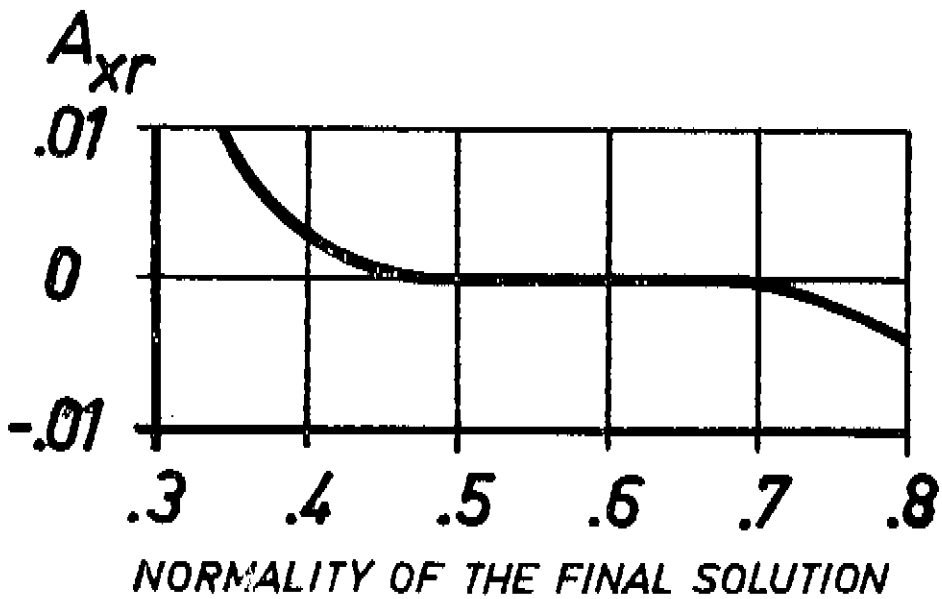


Figure 5. Remedy alternative 2 a

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Sweden

Dahlgren

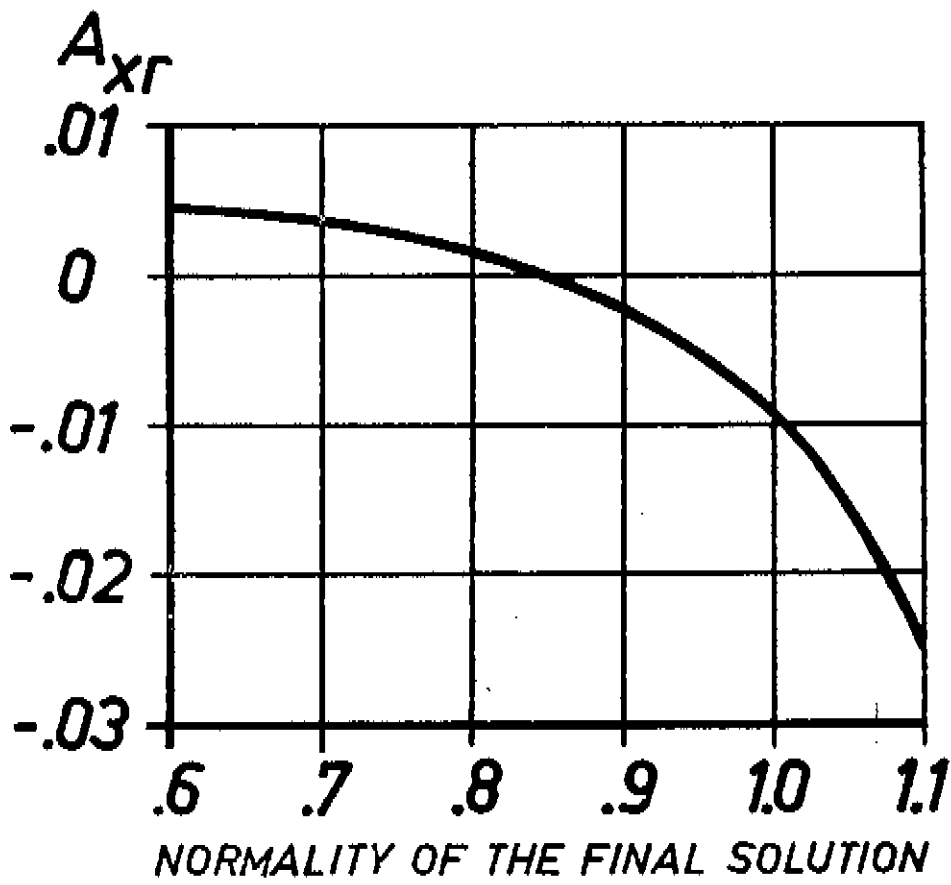


Figure 6. Remedy alternative 2 b

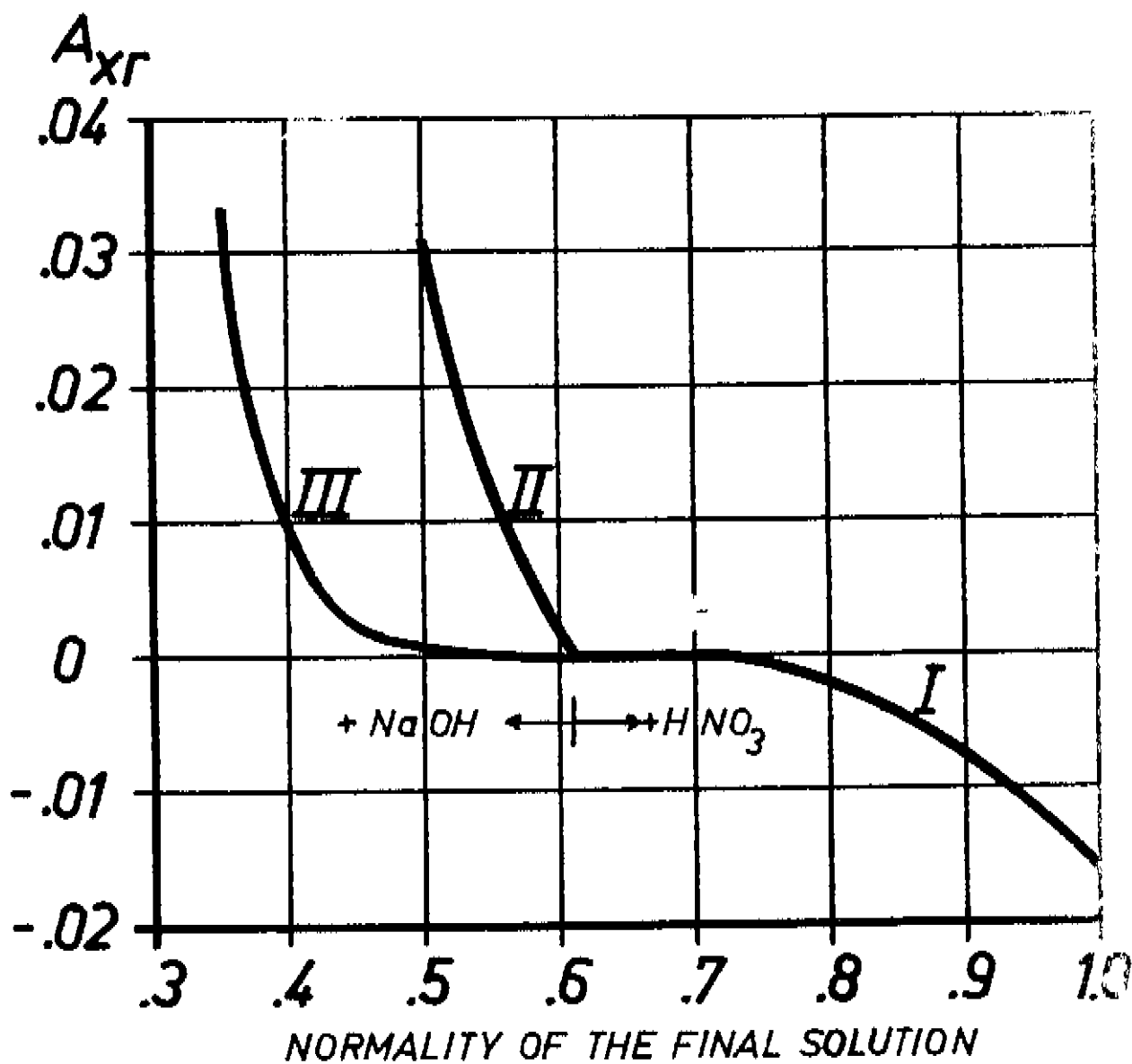


Figure 7. Deviations from normal conditions when adding nitric acid and sodium hydroxide

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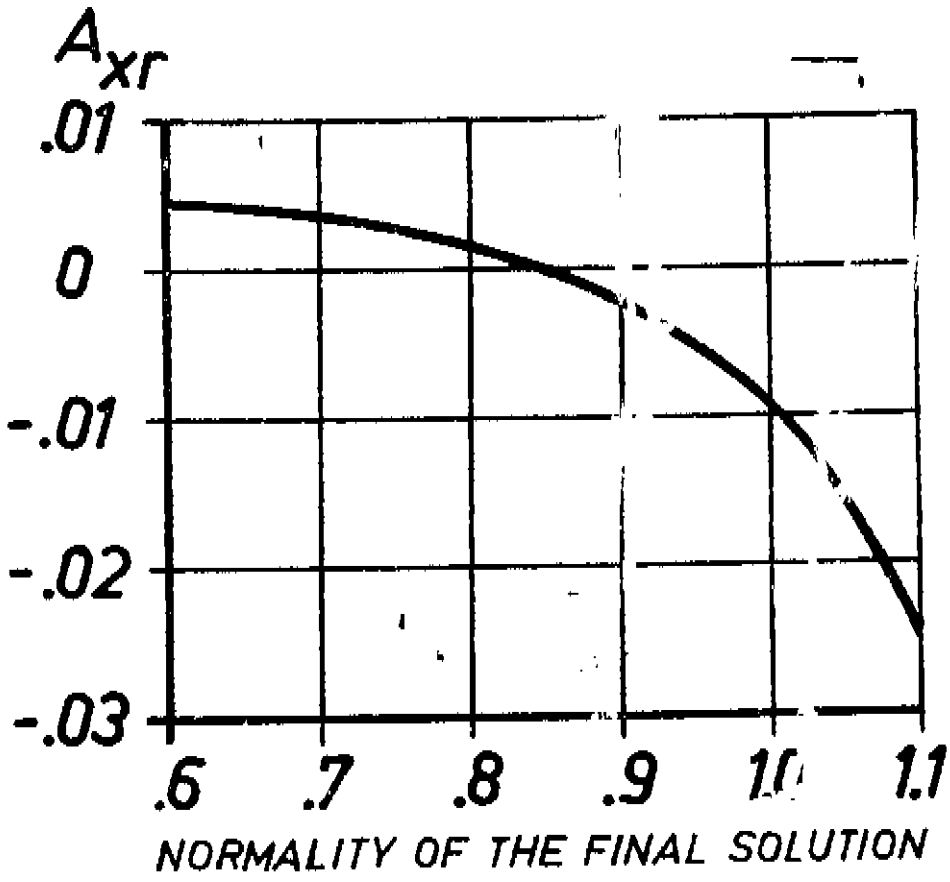


Figure 6. Remedy alternative 2 b

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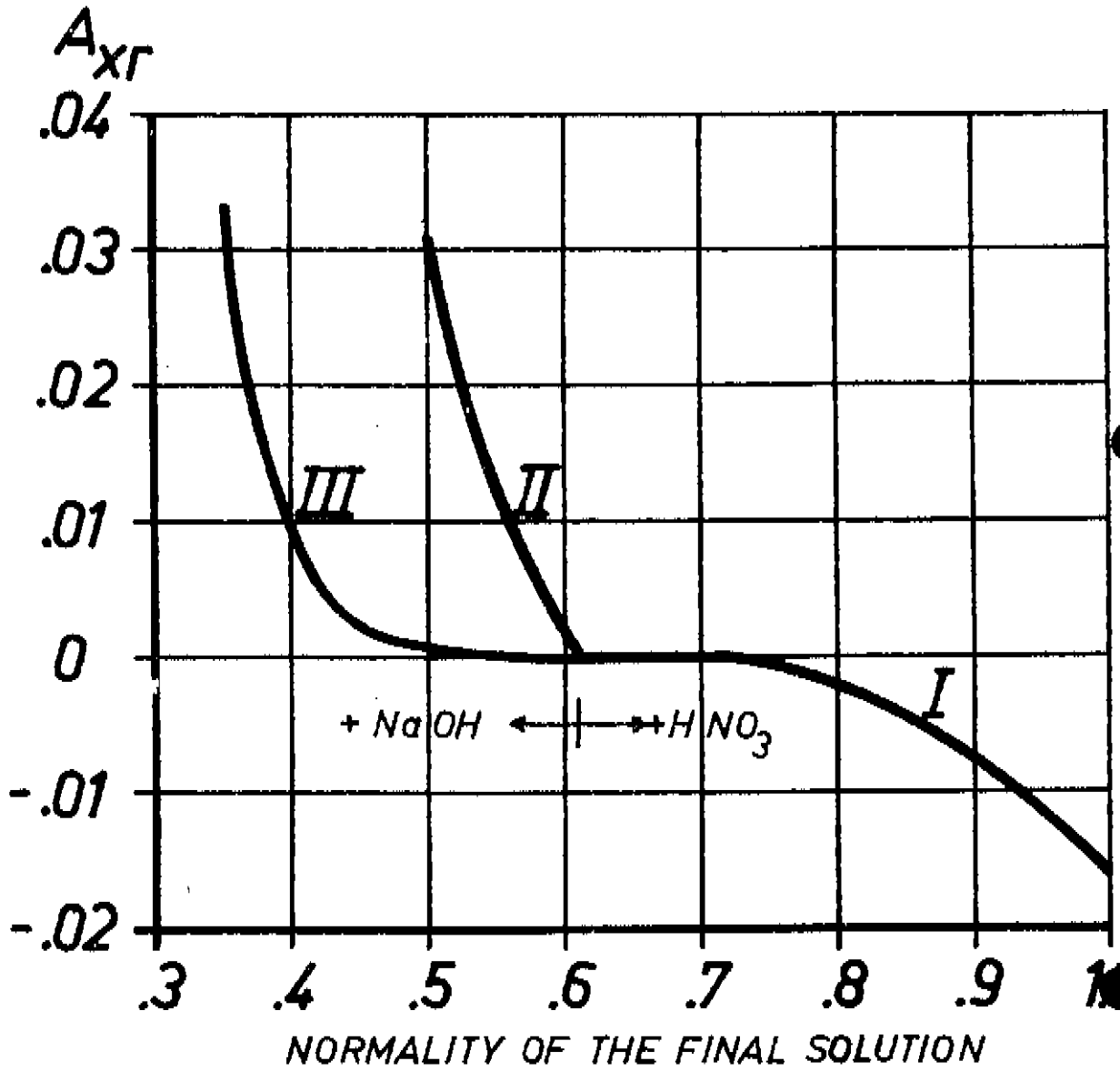


Figure 7. Deviations from normal conditions when adding nitric acid and sodium hydroxide

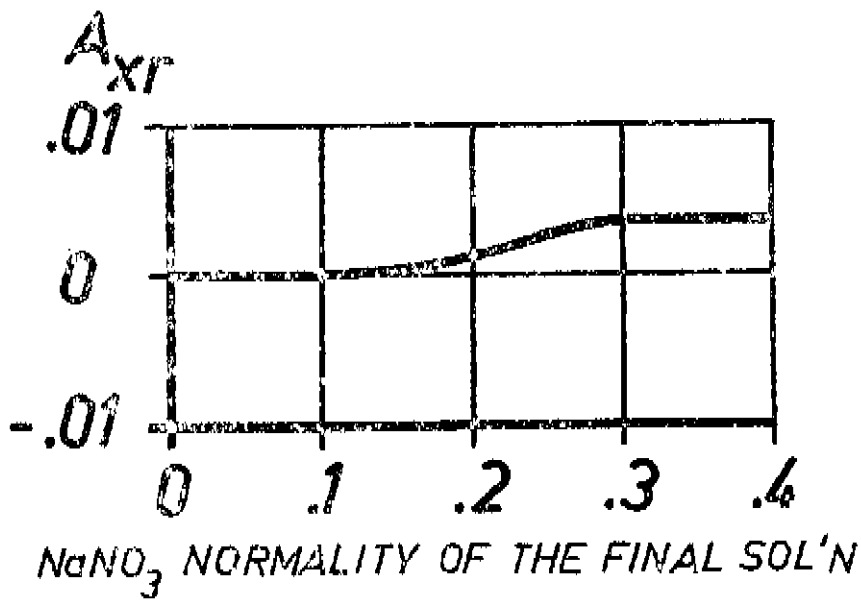


Figure 8. Influence on the relative absorbance
by addition of sodium nitrate

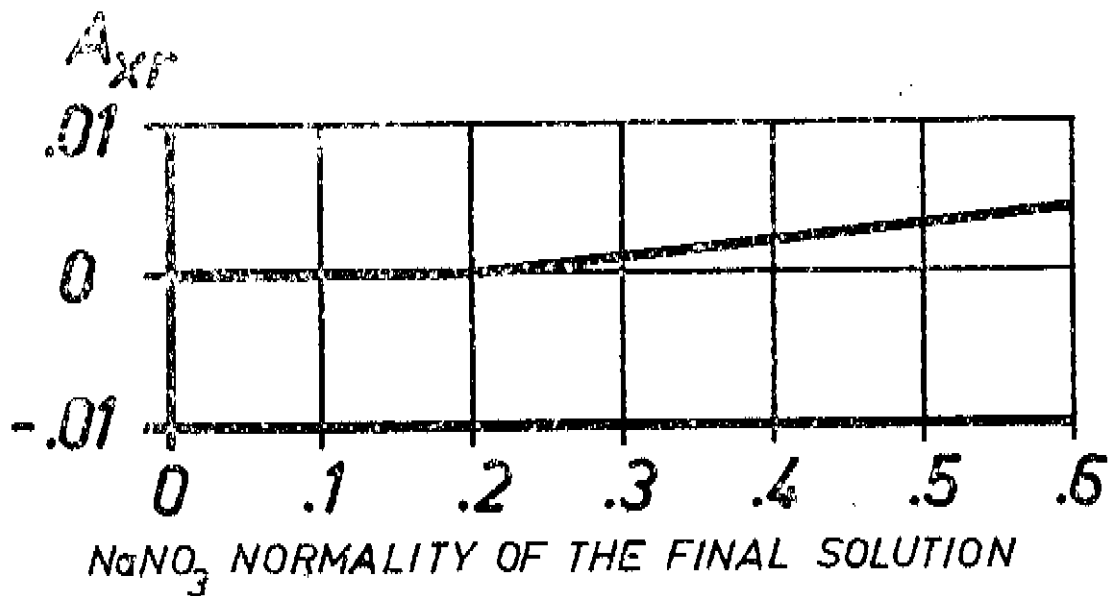


Figure 9. Influence on the relative absorbance by addition of
sodium nitrate, when the acidity of the sample solution
has been increased by .05 normals

0.000-1000

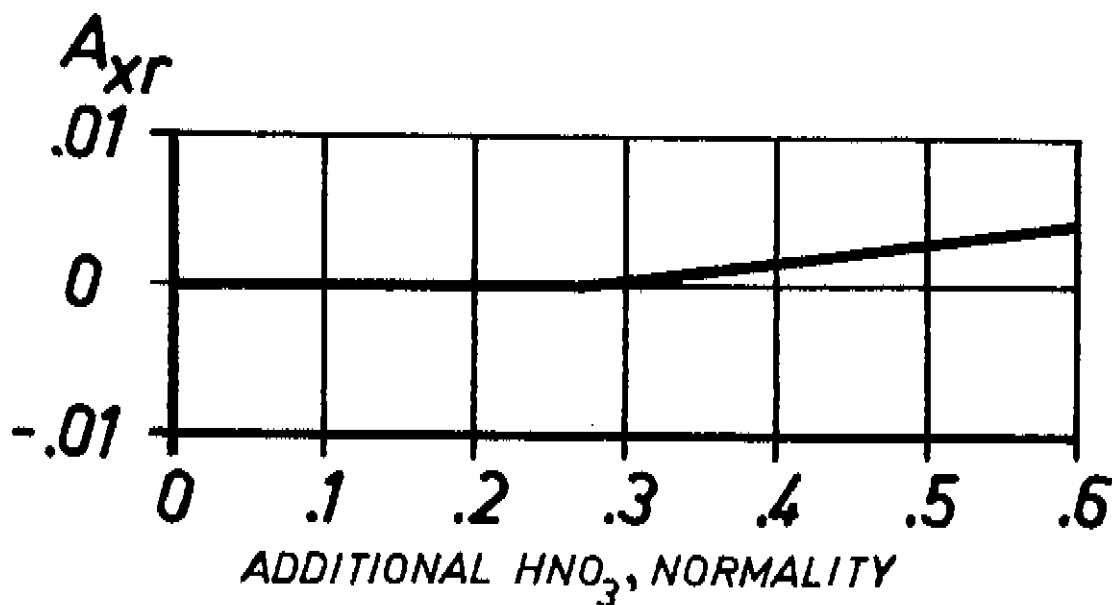


Figure 10. Influence on the relative absorbance by additional nitric acid when neutralised after addition of reagent solution

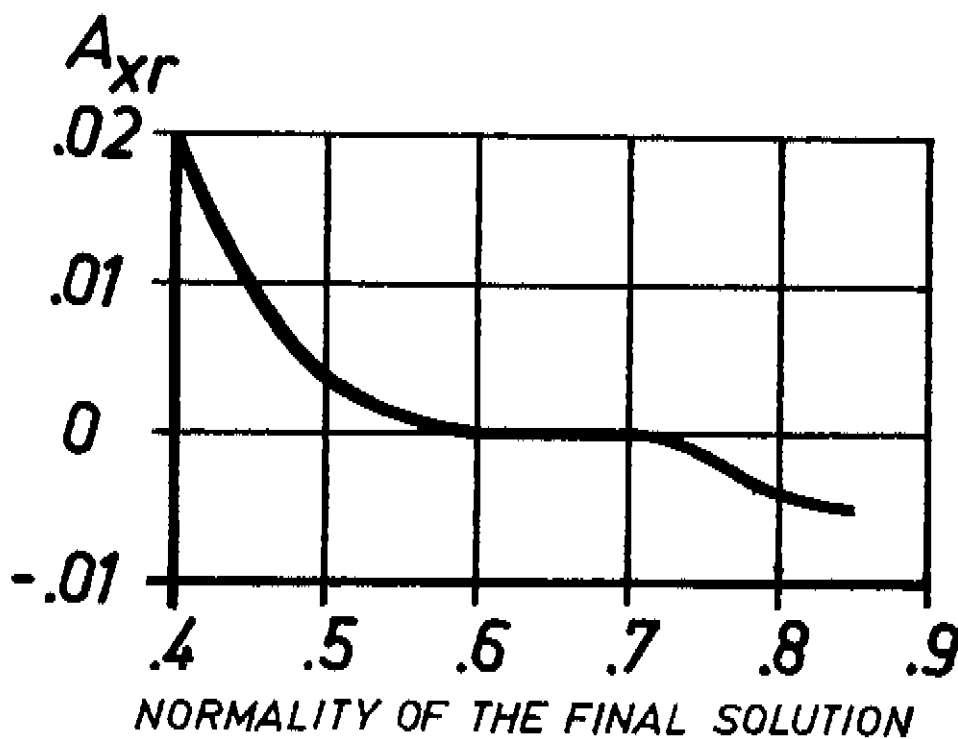


Figure 11. Influence on the relative absorbance by resulting acid normality in the final colored solution, when 24 milliequivalents extra acid has been introduced and neutralised by varying amounts of sodium hydroxide