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МЕЖДУНАРОДНАЯ ОРГАНИЗАЦИЯ ПО СТАНДАРТИЗАЦИИ

Photography — Processing waste — Determination of total amino nitrogen — Microdiffusion Kjeldahl method

Photographie — Effluents de traitements — Détermination de l'azote amino total — Méthode de microdiffusion Kjeldahl

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Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work.

Draft International Standards adopted by the technical committees are circulated to the member bodies for approval before their acceptance as International Standards by the ISO Council. They are approved in accordance with ISO procedures requiring at least 75 % approval by the member bodies voting.

International Standard ISO 6851 was prepared by Technical Committee ISO/TC 42, *Photography*.

Users should note that all International Standards undergo revision from time to time and that any reference made herein to any other International Standard implies its latest edition, unless otherwise stated.

Photography — Processing waste — Determination of total amino nitrogen — Microdiffusion Kjeldahl method

1 Scope

This International Standard specifies a method for determining the total organic nitrogen as well as any ammoniacal nitrogen present in photographic processing wastes by the Kjeldahl method. This amino nitrogen is converted to ammonia, which is subsequently determined by absorption into boric acid in a microdiffusion cell along with any ammonia originally present.

2 Field of application

Total Kjeldahl nitrogen can be determined in photographic processing wastes in the range 10 to 200 mg/l as ammonia or in the range 8 to 160 mg/l in terms of nitrogen. If the ammoniacal nitrogen (see ISO 6853) is determined separately and subtracted, the organic amino nitrogen content can be established.

3 References

ISO 648, *Laboratory glassware — One-mark pipettes.*

ISO 1042, *Laboratory glassware — One-mark volumetric flasks.*

ISO 5667, *Water quality — Sampling —*

Part 1: Guidance on the design of sampling programmes.

Part 2: Guidance on sampling techniques.

Part 3: Guidance on the preservation and handling of samples.

ISO 6853, *Photographic processing wastes — Determination of ammoniacal nitrogen content — Microdiffusion method.*

4 Principle

In the presence of sulfuric acid, potassium sulfate and mercuric sulfate as catalyst, the amino nitrogen of most organic substances is converted into ammonium hydrogen sulfate. The ammonia is then liberated by treatment with a suitable alkali and absorbed into a solution of boric acid. The liberation and absorption of the ammonia is carried out in a microdiffusion cell. The ammonia absorbed into the boric acid is then determined by titration with standard sulfuric acid.

5 Reactions

$$\left.\begin{array}{l}\ldots - NH_2\\ \ldots - NHR\\ \ldots - NR_2\end{array}\right\} + H_2SO_4 \rightarrow (NH_4)HSO_4$$

$$(NH_4)HSO_4 + 2OH^- \rightarrow NH_3 + 2H_2O + SO_4^{--}$$

6 Reagents

Reagents shall be handled in conformity to health and safety precautions as shown on containers or as given in other sources of such information. The discharge of reagents shall conform to applicable environmental regulations.

WARNING

— Sulfuric acid, potassium hydroxide and sodium hydroxide are corrosive and cause burns. Avoid contact with eyes, skin and clothing.

— Mercury(II) oxide may be fatal if swallowed. Harmful by inhalation.

— Methanol is flammable. Keep away from heat, sparks and open flame. Harmful if swallowed.

Reagents used in the tests shall be certified reagent grade chemicals or chemicals of a purity acceptable for the analysis. The acids and ammonia solution referred to shall be undiluted unless dilution is specified. Dilution is specified in terms of amount-of-substance concentration when standardization is required.

Distilled water, or water otherwise produced of at least equal purity, shall be used whenever water is required.

6.1 Acidified mercury(II) sulfate/potassium sulfate solution, $c(HgO) = 2$ g/l, $c(K_2SO_4) = 134$ g/l.

Weigh 134 ± 0,1 g of potassium sulfate (K_2SO_4) and transfer it quantitatively to a 1 000 ml volumetric flask conforming to Class A of ISO 1042. Add about 650 ml of water and dissolve. Carefully add 200 ml of concentrated sulfuric acid from a graduated measuring cylinder and mix. Weigh 2 ± 0,1 g of red mercury(II) oxide (HgO) and dissolve it in 25 ml of 3 mol/l

sulfuric acid in a small beaker. Add the contents of the beaker to the acid potassium sulfate solution, and rinse the beaker into the flask. Dilute the solution to volume when cool, and mix well. Store this solution at a temperature above 14 °C to prevent crystallization.

The 3 mol/l sulfuric acid is prepared by carefully adding 170 ml of concentrated (18 mol/l) sulfuric acid to 500 ml of water in a 1 000 ml volumetric flask, mixing, cooling, and making up to 1 000 ml with water.

6.2 Potassium tetraborate solution, 514 g/l.

Weigh 673 ± 0,1 g of potassium tetraborate ($K_2B_4O_7 \cdot 4H_2O$) and dissolve in 550 ml of water in a 1 000 ml beaker. Then weigh 247 ± 0,1 g of potassium hydroxide (KOH) and dissolve it in the tetraborate solution. Boil on a hotplate for 5 min, cool and add 5 ml of a 10 % aqueous solution on nonylphenoxypoly (6-10) ethylene oxide (NPPO) or similar wetting agent[1]. Transfer to a 1 000 ml volumetric flask, rinsing the beaker into the flask several times. When cool, dilute to volume and mix well. Note that the wetting agent will separate out on standing, so that the flask must be shaken vigorously before each use.

6.3 Boric acid absorbent solution.

Add about 800 ml of water to a 1 000 ml volumetric flask. Stir using a magnetic stirrer and add 2 to 3 mg of Xylene Cyanole FF, weighed to the nearest 1 mg, followed by 0,5 ml of NPPO, followed by 5,0 ml of methyl red indicator solution prepared by dissolving 0,125 g of methyl red in 250 ml of methanol. Add 6 ± 0,1 g of boric acid (H_3BO_3), keeping the contents of the flask stirred until all the constituents are dissolved. Dilute to within about 15 ml of the mark and mix. Place 1,5 ml of this solution in the centre of a micro-diffusion cell and observe the colour.

If the colour in the cell is pink, add just sufficient 0,1 mol/l sodium hydroxide solution to the solution in the 1 000 ml flask to obtain a neutral colour when 1 ml is viewed in the microdiffusion cell.

Check that excess sodium hydroxide is absent by adding 0,10 ml of 0,002 50 mol/l sulfuric acid (6.4) to 1 ml of solution, at which point a pink colour should be produced. Note that the solution in the 1 000 ml flask will appear red, even when 1 ml in the microdiffusion cell looks neutral.

6.4 Sulfuric acid solution, $c(H_2SO_4) = 0{,}002\ 50$ mol/l.

Pipette 50,0 ml of standard volumetric 0,050 00 mol/l sulfuric acid into a 1 000 ml volumetric flask and dilute to volume with water.

6.5 Cleaning solutions for microdiffusion cells.

6.5.1 Cleaning solution A

Add to a 2 000 ml beaker, from a graduated measuring cylinder, about 750 ml of water and about 750 ml of 0,5 mol/l sulfuric acid and stir. Continue stirring and add 2 to 3 ml of household liquid dishwashing detergent and 1 ml of methyl red indicator solution.

6.5.2 Cleaning solution B

Add to a 2 000 ml beaker about 1 500 ml of water and 2 to 3 ml of the detergent and mix. Add 10 ml of 1,0 mol/l sodium hydroxide and then add enough methyl red indicator solution, while stirring, to produce a yellow colour.

6.5.3 Cleaning solution C

Add to a 2 000 ml beaker about 1 500 ml of water and about 5 ml of the detergent and stir. Continue to stir and add about 10 ml of 0,05 mol/l sulfuric acid and enough methyl red indicator to produce a pink colour.

6.6 Standard nitrogen samples (to check ammonia liberation technique).

Dry ammonium chloride for 2 h in an oven at 100 °C and allow to cool in a desiccator before weighing. Weigh 3,819 ± 0,001 g of this ammonium chloride and quantitatively transfer to a 1 000 ml volumetric flask. Dissolve in water and dilute to volume. This stock solution is equivalent to 0,071 4 mol of nitrogen per litre (1,00 mg/ml) and is stable for at least 3 months.

Pipette 10 ml of this stock solution into a 100 ml volumetric flask and dilute to the mark with water. This standard solution is equivalent to 0,007 14 mol of nitrogen per litre (100 mg/l).

In a similar manner, prepare a standard solution equivalent to 0,001 428 mol of nitrogen per litre (200 mg/l), by pipetting 2,00 ml of the stock solution into a 100 ml volumetric flask and dilute to the mark with water.

7 Apparatus

Ordinary laboratory apparatus and

7.1 Kjeldahl digestion rack.

7.2 Kjeldahl flasks, 100 ml capacity.

7.3 Macro-set pipette, capable of delivering 4,00 ml.

7.4 Glass beads, 4 mm diameter.

7.5 One-mark volumetric flask, capacity 25 ml, conforming to ISO 1042 equipped with suitable ground glass stopper.

7.6 Microdiffusion cell, 83 mm, Obrink microdiffusion.

7.7 One-mark pipette, 0,500 ml capacity conforming to ISO 648.

1) Non-ionic detergent with a hydrophilic lipophilic balance in the range 13 to 14.

7.8 Syringe pipette, 1,00 ml capacity.

7.9 Syringe micro-burette.

7.10 Syringe, to deliver 1,50 ml.

7.11 Polytetrafluoroethylene-coated magnetic bar, 7 mm × ø2 mm.

8 Procedure

Samples shall be taken and preserved in accordance with ISO 5667.

8.1 Digestion of sample

Ensure that the digestion rack fume duct is connected to an aspirator through a water trap with water running down the sink while the apparatus is in use. Turn the aspirator on fully. Pipette 25 ml of the sample into a 100 ml Kjeldahl digestion flask (7.2), and add 4,00 ml of the acidified mercuric sulfate/potassium sulfate solution (6.1), using the macro-set pipette (7.3). Add two glass beads (7.4), mix well, and position the flask in the digestion rack (7.1), ensuring that the neck is correctly positioned in the fume duct. Digest at moderate to high temperature until all the water is driven off, and continue digestion for at least 30 min after the evolution of SO_3 commences. If, after this treatment, the residue is coloured, continue the digestion until it becomes colourless and for a further 20 min. Any material spattered onto the walls or neck should be removed by swirling the flask. When digestion is complete, allow to cool and then quantitatively transfer the contents to a 25 ml volumetric flask (7.5). Dilute to the mark with water and insert the glass stopper. Mix well by inverting.

8.2 Cleaning microdiffusion cells and covers

Soak the cells and covers in cleaning solution A (6.5.1) for 1 h; then remove and soak in cleaning solution B (6.5.2) for 1 h; then remove and soak in solution C (6.5.3) for 1 h.

Remove the cells and covers, shake them as dry as possible and invert them to dry on a clean towel.

Do not touch the insides of the clean cells and covers.

If the cleaned cells and covers have not been washed on the day they are to be used, rinse them with distilled water and set them on a clean towel to dry before using.

8.3 Liberation of ammonia from samples

Using a syringe (7.10) add 1,50 ml of the boric acid absorbent (6.3) to the centre of the microdiffusion cell (7.6). Using a 1,00 ml syringe pipette (7.8) add 1,00 ml of the 2,2 mol/l potassium tetraborate (6.2) to the outer sealing chamber and 1,00 ml to the sample chamber (the second chamber from the outside). The tetraborate solution should be vigorously shaken before sampling in order to distribute the NPPO. Great care should be taken not to splash any tetraborate into the centre chamber. If this occurs, a green coloration will be produced, and the sample shall be discarded. The tetraborate should be deposited on only one part of the sample chamber. Leave enough space for the sample to be added without mixing until the cell is sealed.

Using a calibrated 0,500 ml one-mark pipette (7.7) carefully add 0,500 ml of the sample to the empty side of the sample chamber. Cover the cell immediately and rotate the cover to spread the tetraborate and form a good seal. Using a rotary tipping motion, mix the sample with the tetraborate for 30 s, making certain that the sample and absorbent chambers are fully covered but that the contents of the separate chambers do not mix. Leave the cell to stand for 2 h. Longer standing times will not introduce any error.

8.4 Titration

Remove the lid carefully from the cell and place the cell on a magnetic stirrer. Place the magnetic bar (7.11) in the centre chamber without splashing. Using the syringe micro-burette (7.9), titrate the solution in the centre chamber with the 0,002 50 mol/l sulfuric acid (6.4) to the first pink colour. Keep the burette tip immersed while titrating. Stir for about 15 s. If the colour fades to light green, continue to titrate until the pink colour remains for at least 15 s. Let the volume used for titration be V_1.

8.5 Blank reading and a calibration curve check

Concurrently with the sample to be analysed, run procedures 8.1, 8.2 and 8.3 on 0,500 ml of distilled water, on 0,500 ml of the 0,007 14 mol/l standard nitrogen sample and the 0,001 428 mol/l standard nitrogen sample. Let the volume used for the titration on the blank be V_2; on the 0,007 14 mol/l (100 mg of nitrogen per litre) V_3 and on the 0,001 428 mol/l (200 mg of nitrogen per litre) V_4.

9 Expression of results

9.1 Method of calculation

Total Kjeldahl nitrogen (as N), in milligrams per litre, is given by the formula

$$\frac{72{,}6\,(V_1 - V_2)}{V_s}$$

where

V_1 is the volume, in millilitres, used for the titration of the sample;

V_2 is the volume, in millilitres, used for the titration of the water blank;

V_s is the volume, in millilitres, of the sample taken for diffusion.

If V_s is 0,500 ml, the formula becomes

$$145\,(V_1 - V_2)$$

If the digested sample (25 ml) must be further diluted multiply the result above by

$$\frac{\text{ml final dilution volume}}{\text{ml sample diluted}}$$

As a check on the precision, perform similar calculations on the results ($V_3 - V_2$) and ($V_4 - V_2$) for the two standard nitrogen samples. These should be carried out for each set of effluent samples or at least daily. The conformance of these results to levels as prepared indicates the probable reliability of the results on unknown samples.

Total organic nitrogen (N) = total Kjeldahl nitrogen − ammoniacal nitrogen

9.2 Precision

The 95 % confidence limits for a single determination are expected to be between 4 and 8 mg of nitrogen per litre. The stoichiometric yield by the microdiffusion method is about 96 %.

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