G-47-01

International Standard ISO 7525

INTERNATIONAL ORGANIZATION FOR STANDARDIZATION•МЕЖДУНАРОДНАЯ ОРГАНИЗАЦИЯ ПО СТАНДАРТИЗАЦИИ•ORGANISATION INTERNATIONALE DE NORMALISATION

Nickel — Determination of sulfur content — Methylene blue molecular absorption spectrometric method after generation of hydrogen sulfide

Nickel — Dosage du soufre — Méthode spectrométrique par absorption moléculaire au bleu de méthylène après distillation d'acide sulfhydrique

First edition — 1985-12-01

UDC 669.24 : 543.422 : 543.845 **Ref. No. ISO 7525-1985 (E)**

Descriptors : nickel, chemical analysis, determination of content, sulfur, spectrochemical analysis.

Price based on 6 pages

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 7525 was prepared by Technical Committee ISO/TC 155, *Nickel and nickel alloys.*

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.

Printed in Switzerland

Nickel — Determination of sulfur content — Methylene blue molecular absorption spectrometric method after generation of hydrogen sulfide

1 Scope and field of application

This International Standard specifies a molecular absorption spectrometric method after generation of hydrogen sulfide for the determination of the sulfur content of refined nickel in the range 0,000 1 to 0,002 % (*m*/*m*).

2 Reference

ISO 5725, *Precision of test methods — Determination of repeatability and reproducibility by inter-laboratory tests.*

3 Principle

Dissolution of a test portion in a nitric acid-chloric acid mixture and oxidation of total sulfur to sulfate ion. Removal of nitrates by evaporation with hydrochloric and formic acids. Reduction of sulfate to hydrogen sulfide by hydroiodic and hypophosphorous acids in an argon atmosphere.

Absorption of the hydrogen sulfide by a zinc ammine complex solution. Conversion of absorbed sulfide sulfur to methylene blue and measurement of absorbance of the solution at 665 nm. Determination of the mass of sulfur from a calibration graph.

4 Reagents and materials

During the analysis, unless otherwise stated, use only reagents of recognized analytical grade and only distilled water or water of equivalent purity.

All acids used in the dissolution of the test portion and the nitrate removal step shall be purified by distillation to eliminate sulfur-containing species, such as sulfur dioxide and sulfuric acid. Impurity levels of 1 mg of sulfur per litre are not sufficiently low. To keep the blank test sulfur content low, hydrochloric acid, in particular, should contain less than 0,05 mg of sulfur per litre.

4.1 Hydrochloric acid, ρ_{20} = 1,18 g/ml, diluted 1 + 4.

4.2 Purified hydrochloric acid, ρ_{20} = 1,098 g/ml.

Distil hydrochloric acid (ρ_{20} = 1,18 g/ml) diluted 3 + 2 with water using the apparatus shown in figure 1 and discard the first 10 % (*V*/*V*) of the distillate. Collect the remaining distillate (except for the last few millilitres) in a thoroughly cleaned glass bottle.

4.3 Purified formic acid, ρ_{20} = 1,20 g/ml.

Distil formic acid using the apparatus shown in figure 1 and discard the first 10 % (*V*/*V*) of the distillate. Collect the remaining distillate (except for the last few millilitres) in a thoroughly cleaned glass bottle.

4.4 Nitric acid-chloric acid mixture.

4.4.1 Distil nitric acid (ρ_{20} = 1,41 g/ml) using the apparatus shown in figure 1 and discard the first 10 % (*V*/*V*) of the distillate. Collect the remaining distillate (except for the last few millilitres) in a thoroughly cleaned brown glass bottle.

4.4.2 Dissolve 3 g of potassium chlorate ($KClO_3$) in 30 ml of water and add 100 ml of purified nitric acid (4.4.1). Prepare fresh as needed.

4.5 Zinc acetate, absorbing solution.

Dissolve 5 g of zinc acetate dihydrate [$Zn(CH_3COO)_2 \cdot 2H_2O$] and 70 g of ammonium chloride (NH_4Cl) in about 350 ml of water. Add 7,5 g of sodium hydroxide (NaOH), stir to dissolve, and dilute to 500 ml with water.

Store in a glass bottle.

4.6 Reducing mixture

Transfer 420 ml of hydroiodic acid [ρ_{20} = 1,7 g/ml, 55 % (*m*/*m*) HI minimum], 80 ml of hypophosphorous acid [ρ_{20} = 1,21 g/ml, 50 % (*m*/*m*) H_3PO_2 minimum] and 70 g of sodium iodide to the purifying apparatus (see figure 2). Attach the hydrogen sulfide trap containing 50 ml of the absorbing solution (4.5). Purge with argon at a flow rate of 200 to 300 ml/min for 10 min to expel air from the system. Switch on the electric heating mantle and heat the mixture at 113 to 115 °C for 4 h in a continuous flow of argon. Allow the mixture to cool while maintaining the argon flow.

Transfer the cold reducing mixture, without delay, to a brown glass bottle. Stopper and store in a cool dark place. (See clause 9.)

4.7 Diamine salt, solution.

Dissolve 0,1 g of *N, N*-dimethyl-*p*-phenylenediamine hydrochloride or sulfate in 25 ml of hydrochloric acid (ϱ_{20} = 1,18 g/ml) and dilute to 100 ml with water.

Store in a cool dark place.

Prepare fresh weekly.

4.8 Iron(III) chloride, solution.

Dissolve 1,0 g of iron(III) chloride hexahydrate ($FeCl_3 \cdot 6H_2O$) in 10 ml of hydrochloric acid (ϱ_{20} = 1,18 g/ml) and 40 ml of water. Dilute to 100 ml with water.

Store in a glass bottle.

4.9 Sulfur, standard solution, corresponding to 100 mg of S per litre.

Dissolve exactly 0,543 5 g of potassium sulfate, previously dried at 105 °C for 1 h, in water in a 1 000 ml one-mark volumetric flask. Make up to the mark with water and mix.

1 ml of this standard solution contains 0,100 mg of S.

4.10 Argon 99,998 % (*m/m*) Ar minimum.

5 Apparatus

Ordinary laboratory glassware, and

5.1 Distillation apparatus, for the generation and volatilization of hydrogen sulfide from the test solution, as shown in figure 3. The double surface condenser is preferred because of its superior cooling efficiency.

5.2 Heating mantle. The optimum temperature for a rapid reduction of sulfate to hydrogen sulfide is around 114 °C. The solution would then reflux very gently. The required power setting for the mantle shall be established by preliminary blank tests with a thermometer dipped in the heated solution.

5.3 Molecular absorption spectrometer, suitable for measuring absorbance at 665 nm.

5.4 Micropipettes, of capacities 10; 20; 50; and 100 µl.

6 Sampling and samples

6.1 Sampling and preparation of the laboratory sample shall be carried out by normal agreed procedures or, in case of dispute, by the relevant International Standard.

6.2 The laboratory sample normally is in the form of a powder, granules, millings or drillings and no further preparation of the sample is necessary.

6.3 If it is suspected that the laboratory sample is contaminated with oil or grease from the milling or drilling process, it shall be cleaned by washing with high purity acetone and drying in air.

6.4 If the laboratory sample contains particles or pieces of widely varying sizes, the test portion should be obtained by riffling.

7 Procedure

WARNING — **There are toxicity risks related to the chemicals used in the procedure and reasonable precautions shall be taken. The glassware used in the distillation apparatus shall be examined carefully and its performance and tightness of joints checked.**

7.1 Test portion and preparation of test solution

7.1.1 Weigh, to the nearest 0,01 g, 1,0 g of the test sample and transfer to a 100 or 250 ml three neck round bottom flask. Add 10 ml of nitric acid-chloric acid mixture (4.4) and allow the reaction to subside. Carefully evaporate the solution to a viscous syrup.

7.1.2 Add 10 ml of purified hydrochloric acid (4.2) and heat to dissolve the residue. Add 2 ml of formic acid (4.3) and evaporate to dryness. Dissolve the dry residue in 10 ml of purified hydrochloric acid and 0,5 ml of formic acid. Heat and mineralize for a few minutes on the hotplate to complete dissolution and cool.

NOTES

1 It is essential that all sample treatment be carried out in a scrupulously clean laboratory atmosphere, i.e. free from sulfuric acid fumes and any vapours or dust containing sulfur species. Dissolution of the test portion in the three neck flask, rather than a beaker, reduces the chance of contamination.

2 The three neck flask may be held in a cylindrical metal holder for heating on a hotplate. A sand-bath on a hotplate may also be used. Alternatively the flask may be suspended in a low-form beaker of suitable size.

3 If brown fumes appear during the final dissolution, evaporate to dryness again and dissolve the residue in hydrochloric and formic acids as indicated in 7.1.2.

7.2 Hydrogen sulfide evolution

7.2.1 Attach the three neck flask to the distillation apparatus (5.1). Place 3 ml of hydrochloric acid diluted 1 − 4 into the acid trap, and 5,0 ml of absorbing solution (4.5) into the hydrogen sulfide trap. Add 30 ml of the reducing mixture (4.6) to the sample solution via the side arm. Replace the stopper.

7.2.2 Ensure that all joints are secure and pass a flow of argon (4.10) through the apparatus at a rate of 30 ml/min. After approximately 2 min switch on the heating mantle and continue heating for 30 min. Remove the sulfide trap and switch off the heating mantle.

7.3 Methylene blue development

7.3.1 Introduce 3,0 ml of the diamine salt solution (4.7) into the sulfide trap via the gas inlet tube. Immediately follow with addition of 0,5 ml of iron(III) chloride solution (4.8) and mix gently.

7.3.2 Rinse the inside and outside of the gas inlet tube with a small quantity of water. Mix the solution and transfer it to a 25 ml one-mark volumetric flask. Wash the test-tube with water. Make up to the mark with water, mix, and allow the solution to stand for at least 30 min before measurement.

NOTE — Once fully developed, the methylene blue coloration is stable for at least 24 h.

7.4 Spectrometric measurement

Measure the absorbance of the solution using 1 or 2 cm cells against water as the reference at a wavelength of 665 nm with the molecular absorption spectrometer (5.3).

7.5 Blank test

7.5.1 Carry out a blank test in the same apparatus, by the same procedure, using the same quantities of all the reagents as in the determination, but omitting the test portion.

7.5.2 Having finished the volatilization of hydrogen sulfide from the blank test as in 7.2.2, allow the now sulfur-free reducing solution to cool in a flow of argon and use it in the calibration (7.6).

7.6 Calibration

7.6.1 To the cold (< 50 °C) sulfur-free reducing mixture (7.5.2) in the three neck flask add, from a micropipette, 10 µl (1 µg S) of sulfur standard solution (4.9). Proceed as directed in 7.2 to 7.4.

7.6.2 Continue with additions, in order of 20; 50; and 100 µl (2; 5; and 10 µg S) of sulfur standard solution (4.9), to the same cold sulfur-free reducing mixture as in 7.6.1.

7.6.3 Plot the absorbance readings of solutions obtained in 7.6.1 and 7.6.2 against the mass, in micrograms, of sulfur present in the solutions. The graph does not have to pass through the origin as the absorbing solution (4.5) usually shows a slight background absorption upon addition of the diamine salt and iron(III) chloride.

8 Expression of results

8.1 Calculation

The sulfur content, expressed as a percentage by mass, of the test portion, is given by the formula

$$\frac{m_1 - m_2}{m_0} \times 10^{-4}$$

where

m_0 is the mass, in grams, of the test portion (7.1);

m_1 is the mass, in micrograms, of sulfur in the test portion, read from the calibration graph (7.6.3);

m_2 is the mass, in micrograms, of sulfur in the blank test, read from the calibration graph (7.6.3).

For a meaningful result, the following condition shall apply: $m_1 \geqslant 2m_2$. If $m_1 < 2m_2$, the reagent blank shall be improved by additional purification of the reagents used. Another possible source for high blanks can be the laboratory environment.

NOTE — A blank value of 0,5 µg sulfur has been found attainable and acceptable.

8.2 Precision

This International Standard was subjected to a limited interlaboratory test programme involving only three laboratories in three countries. Three samples were analysed.

The data were analysed according to ISO 5725 with results given in the table.

Table

Sample reference	C21	C22	C23
Mean sulfur content (g/t)	0,77	3,3	13,1
Standard deviation			
— within laboratory, s_w	0,07	0,12	0,24
— between laboratories, s_b	0,07	0,21	1,35
Repeatability, r	0,19	0,33	0,68
Reproducibility, R	0,26	0,67	3,9

9 Notes on procedure

9.1 Due to the extraordinary sensitivity of the method, the analyst's worst enemies are his/her work habits and the laboratory environment. In practice, it may be useful to provide a room for this type of analysis. If the analyst chooses to run two reagent blanks, the lower one usually is the correct one. Spurious contamination by sulfur has been observed when new three neck flasks, scrupulously cleaned with aqua regia, were used.

9.2 Chemically, the reduction of sulfate to hydrogen sulfide is a difficult reaction. To ensure a complete sulfur recovery, the reaction conditions shall be closely controlled. The optimum reducing temperature is 114 to 116 °C. If the reducing solution is excessively diluted by the sample solution, the boiling point is decreased and the reduction kinetics are slowed appreciably. At temperaturers above 120 °C the acid mixture shows signs of decomposition of hypophosphorous acid and an increased formation of phosphine.

9.3 During the purification of the reducing mixture care shall be taken to ensure that it does not become overheated. Temperature monitoring with a thermometer is recommended. Dilution of 30 ml of the reducing mixture with not more than 10 ml of sample solution will enable the mixture to reflux gently at 114 to 115 °C.

9.4 The volumes of solutions used in the acid trap and the hydrogen sulfide absorber should not be changed from those specified in the procedure as this may result in either a hydrogen sulfide loss or in problems in the acidity dependent development of the methylene blue colour. In the calibration step, there is no need to replace the acid trap solution with a fresh one when the reducing mixture is spiked with the sulfur standard solution.

9.5 The method has been found to produce identical calibration graphs, in absolute terms, on various days.

9.6 The method described in this International Standard is more complex than that in ISO 7526 and is only advised for the analysis of nickel metal not covered by the scope of ISO 7526 or in the absence of the apparatus required for ISO 7526.

10 Test report

The test report shall include the following information:

a) the reference to the method used;

b) the results of the analysis;

c) the number of independent replications;

d) any unusual features noted during the analysis;

e) any operation not included in this International Standard or regarded as optional.

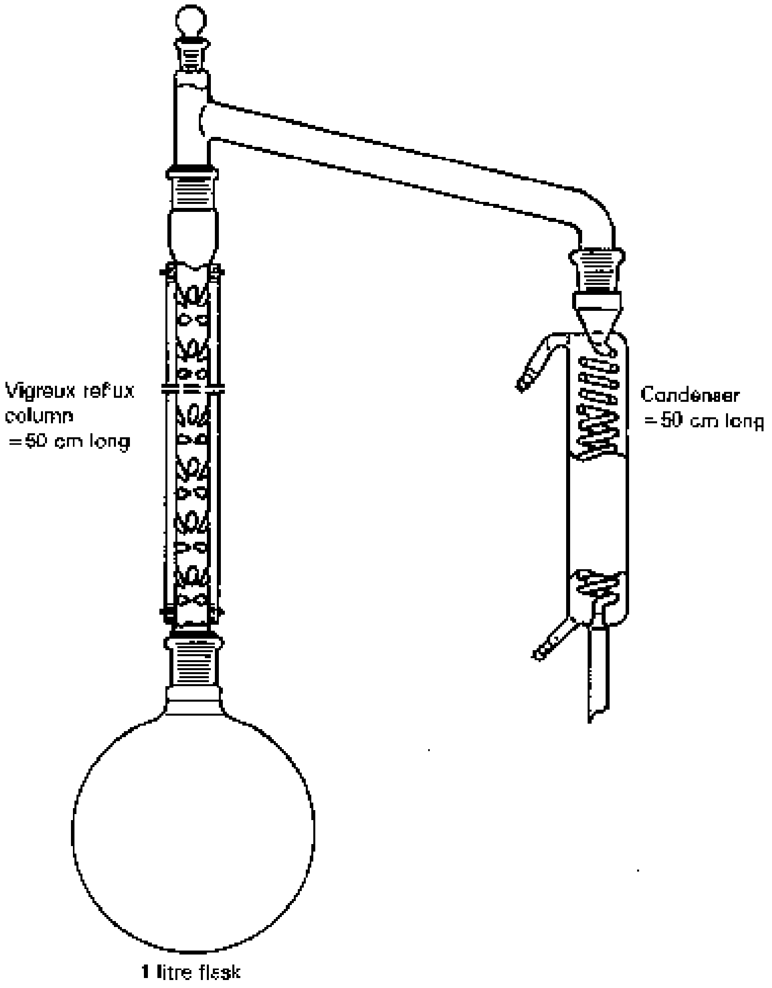

Figure 1 — Apparatus for purification of acids

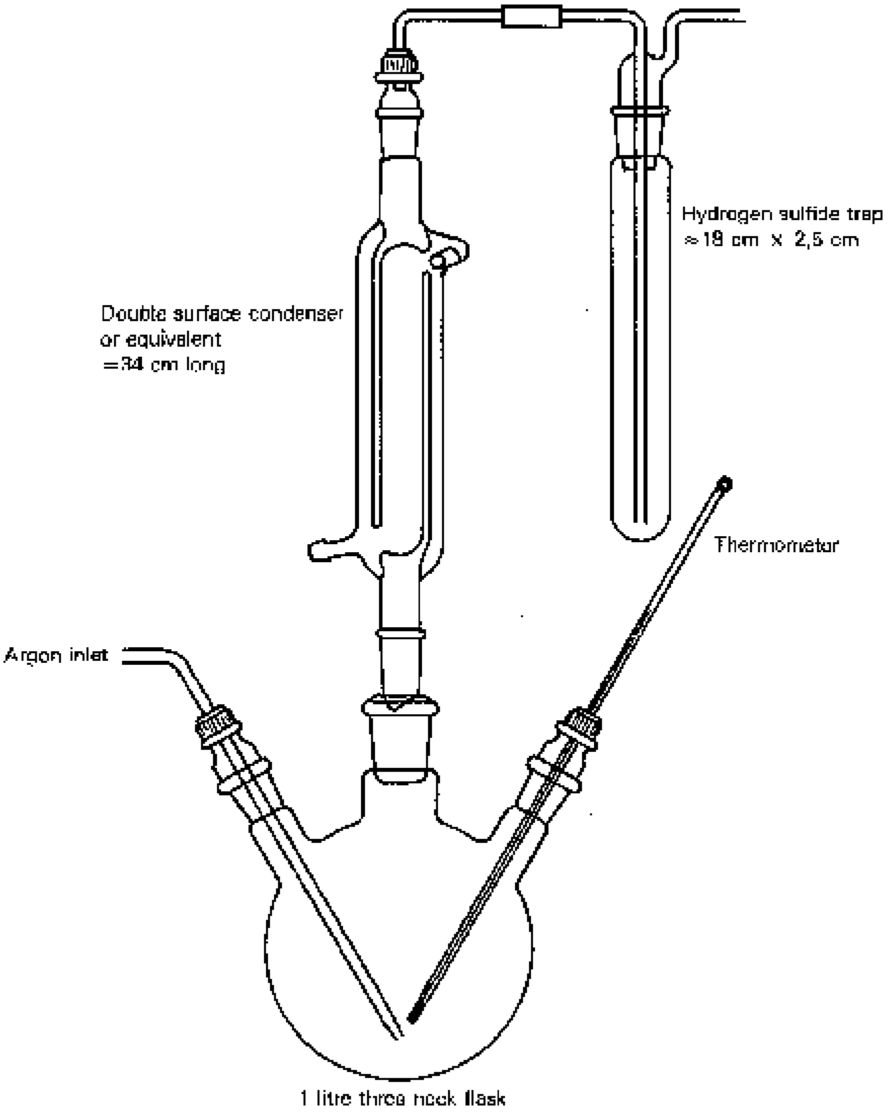

Figure 2 — Apparatus for purification of the reducing mixture

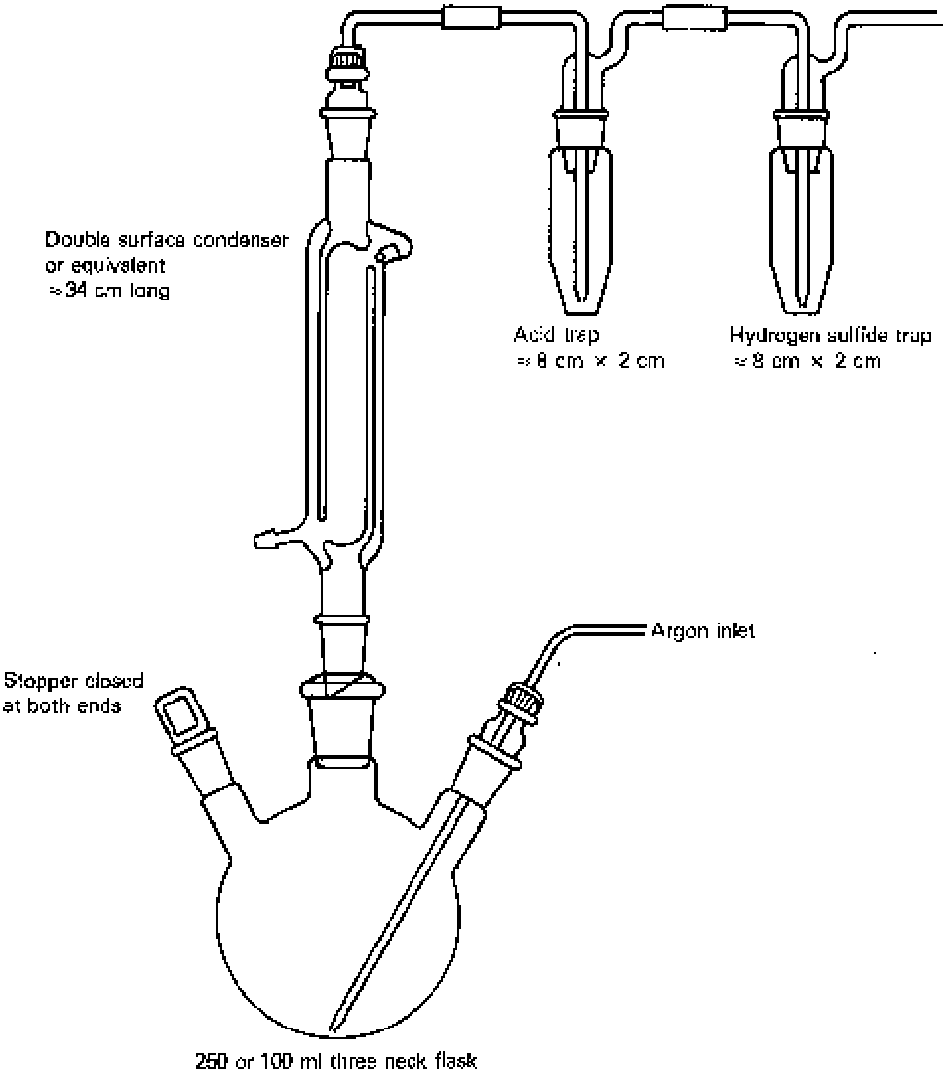

Figure 3 — Apparatus for distillation of hydrogen sulfide