International Standard 6351

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

Nickel — Determination of silver, bismuth, cadmium, cobalt, copper, iron, manganese, lead and zinc contents — Flame atomic absorption spectrometric method

Nickel — Dosage de l'argent, du bismuth, du cadmium, du cobalt, du cuivre, du fer, du manganèse, du plomb et du zinc — Méthode par spectrométrie d'absorption atomique dans la flamme

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Foreword

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Nickel — Determination of silver, bismuth, cadmium, cobalt, copper, iron, manganese, lead and zinc contents — Flame atomic absorption spectrometric method

1 Scope and field of application

This International Standard specifies a flame atomic absorption spectrometric method for the determination of the silver, bismuth, cadmium, cobalt, copper, iron, manganese, lead and zinc contents of refined, wrought and cast nickel within the ranges specified in table 1. This method is applicable to the independent determination of any one or more of the elements listed without including all the elements specified in the standard solutions.

Table 1 — Concentration ranges of elements to be determined

Element	Concentration range, [% (m/m)]*	
	Procedure A	Procedure B
Ag	0,000 2 to 0,01	—
Bi	0,001 0 to 0,01	—
Cd	0,000 2 to 0,002 5	—
Co	0,001 0 to 0,01	0,01 to 1,00
Cu	0,000 2 to 0,01	0,01 to 1,00
Fe	0,002 5 to 0,01	0,01 to 0,15
Mn	0,000 5 to 0,01	0,01 to 0,20
Pb	0,000 5 to 0,01	—
Zn	0,000 2 to 0,002 5	0,00 1 to 0,01 5

* For specific compositions, see ISO 6283.

The lower level for iron can be extended to less than 0,002 5 % (m/m) provided nickel containing less than 0,000 1 % (m/m) iron is used for preparation of standard solutions; see 4.1.

The upper limit for the determination of cobalt and copper can be raised to 2 % (m/m) by a minor modification to the method; see 11.1.

For potential interferences, see clause 10.

2 References

ISO 385/1, *Laboratory glassware — Burettes — Part 1: General requirements.*

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

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

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

3 Principle

Dissolution of a test portion in nitric acid diluted (1 + 1), evaporation of excess acid and dilution of the solution to a known volume.

Aspiration of the solution into the air-acetylene flame of an atomic absorption spectrometer.

Measurement of the absorption of the resonance line energy from the spectrum of each element and comparison with that of calibration solutions of the same element in a matched nickel matrix.

4 Reagents

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

4.1 Nickel powder, high purity containing less than 0,000 5 % (m/m) iron and less than 0,000 1 % (m/m) each of silver, bismuth, cadmium, cobalt, copper, manganese, lead and zinc.

4.2 Nitric acid (HNO_3) ϱ_{20} = 1,41 g/ml, diluted 1 + 1.

The same batch of nitric acid shall be used throughout the procedure.

4.3 Nitric acid (HNO_3) ϱ_{20} = 1,41 g/ml, diluted 1 + 19.

The same batch of nitric acid shall be used throughout the procedure.

4.4 Mixed analyte standard solutions.

4.4.1 Metal stock standard solutions, corresponding to 1,000 g of Ag, Bi, Cd, Co, Cu, Fe, Mn, Pb, or Zn per litre.

Prepare separately for each metal of interest.

Weigh to the nearest 0,001 g, 1,00 g of silver, bismuth, cadmium, cobalt, copper, iron, manganese, lead, or zinc [at least 99,9 % (m/m) pure], transfer to a 600 ml beaker and dissolve in 40 ml of nitric acid (4.2). Heat to complete dissolution, boil gently to expel oxides of nitrogen, cool and transfer to a 1 000 ml one-mark volumetric flask containing 160 ml of nitric acid (4.2). Make up to the mark with water and mix.

Store in polyethylene bottles, except for silver which is stored in glass.

4.4.2 Mixed analyte standard solution A, corresponding to 20 mg each of Ag, Bi, Cd, Co, Cu, Fe, Mn, Pb per litre and 10 mg of Zn per litre.

Pipette 20,0 ml each of the silver, bismuth, cadmium, cobalt, copper, iron, manganese and lead stock standard solutions (4.4.1) and 10 ml of the zinc stock standard solution (4.4.1) into a 1 000 ml one-mark volumetric flask containing 160 ml of nitric acid (4.2). Make up to the mark with water and mix.

Store in a glass bottle.

4.4.3 Mixed analyte standard solution B, corresponding to 100 mg each of Co, Cu, Fe, Mn per litre and 10 mg of Zn per litre.

Pipette 50,0 ml each of the cobalt, copper, iron and manganese stock standard solutions (4.4.1) and 5,0 ml of the zinc stock standard solution (4.4.1) into a 500 ml one-mark volumetric flask. Make up to the mark with water and mix.

Store in a polyethylene bottle.

5 Apparatus

Ordinary laboratory apparatus, and

5.1 Atomic absorption spectrometer.

5.1.1 The atomic absorption spectrometer used in this method shall meet the instrument performance parameters given in annex A.

5.1.2 The instrument shall be equipped with a burner head capable of accepting a solution containing 25 g of Ni as nitrate per litre and suitable for an air-acetylene flame.

5.1.3 The instrument should be capable of using single element hollow cathode or electrodeless discharge lamps operated at currents recommended by the instrument manufacturer.

5.2 Burette, of capacity 50 ml graduated in divisions of 0,1 ml in accordance with ISO 385/1, class A.

5.3 Pipettes, of capacities 5; 20; 25; 50; and 100 ml, in accordance with ISO 648, class A.

5.4 Volumetric flasks, of capacities 200; 250; 500; and 1000 ml, in accordance with ISO 1042, class A.

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 A

This procedure is applicable to 0,000 5 % (m/m) to 0,01 % (m/m) of silver, bismuth, cadmium, cobalt, copper, iron, manganese and lead, and 0,000 5 % to 0,005 % (m/m) zinc.

7.1 Preparation of test solution

Weigh, to the nearest 0,01 g, 4,9 to 5,1 g of the laboratory sample and transfer to a clean unetched 600 ml beaker. Add sufficient water to cover the test portion and dissolve by adding 60 ml of nitric acid (4.2) in small portions. Heat to complete dissolution, boil gently to expel oxides of nitrogen and evaporate to a viscous syrup. Redissolve the salts by adding 20 ml of nitric acid (4.2) and 100 ml of water. Heat to complete dissolution, cool and filter, if necessary, through glass-wool washed with nitric acid (4.2) or a cellulose filter into a 200 ml one-mark volumetric flask. Wash the filter with water. Make up to the mark with water and mix.

If sample inhomogeneity is suspected, a larger test portion, 10 to 50 g, may be taken for analysis. However, an aliquot portion to correspond to a 5 g test portion shall be taken from such a solution and processed in accordance with the procedure given. See 11.2.

7.2 Blank test

The zero member of the set of calibration solutions A (7.3) serves as the blank test since the same batch of nitric acid is used for dissolution of both the nickel reference and test samples.

If it is impossible to use the same batch of nitric acid a second blank test shall be prepared using the same nickel powder (4.1). This blank is then compared with the zero member and an appropriate correction made.

7.3 Preparation of the set of calibration solutions A

7.3.1 This set corresponds to 0; 0,2; 0,5; 1,0; 1,5; 2,0; and 2,5 mg each of Ag, Bi, Cd, Co, Cu, Fe, Mn and Pb per litre and 0; 0,1; 0,25; 0,5; 0,75; 1,0; and 1,25 mg of Zn per litre (see table 2). All the solutions contain a matrix of 25 g of Ni per litre.

Table 2 — Set of calibration solutions A

No.	Volume of mixed analyte standard solution A (4.4.2) (ml)	Analyte concentration (mg/l)	
		Ag, Bi, Cd, Co, Cu, Fe, Mn, Pb	Zn
1	0	0	0
2	2,0	0,2	0,1
3	5,0	0,5	0,25
4	10,0	1,0	0,5
5	15,0	1,5	0,75
6	20,0	2,0	1,0
7	25,0	2,5	1,25

7.3.2 Weigh, to the nearest 0,01 g, seven separate 5,0 g portions of nickel powder (4.1) and transfer to 600 ml beakers. Dissolve as directed in 7.1.

7.3.3 Add, using a burette, 0; 2,0; 5,0; 10,0; 15,0; 20,0; and 25,0 ml respectively of the mixed analyte standard solution A (4.4.2) to the 200 ml flasks. Make up to the mark with water and mix.

7.3.4 The solution with no analyte added is the zero member, which also serves as the blank test (see 7.2).

7.4 Calibration and determination

7.4.1 Spectrometric measurements

7.4.1.1 The spectral lines specified in table 3 should be used in the analysis.

Table 3 — Spectral lines — Procedure A

Element	Ag	Bi	Cd	Co	Cu
Wavelength (nm)	328,1	223,1	228,8	240,7	324,7
Element	Fe	Mn	Pb	Zn	
Wavelength (nm)	248,3	279,5	217,0	213,9	

7.4.1.2 The alternative less sensitive spectral lines specified in table 4 may be used.

Table 4 — Alternative spectral lines — Procedure A

Element	Co	Cu	Fe	Mn	Pb
Wavelength (nm)	241,2	327,4	252,7	403,1	283,3

7.4.1.3 Set the required instrument parameters according to the manufacturer's instructions. Light the burner and aspirate nitric acid diluted (1 + 19) (4.3) until thermal equilibrium is reached. A fuel-lean air-acetylene flame shall be used.

7.4.1.4 Ensure that the instrument meets the performance requirements given in annex A.

NOTE — Optimum settings for the operating parameters vary from instrument to instrument. Scale expansion may have to be used to obtain the required readability.

7.4.1.5 Ensure that the test solution (7.1) and the set of calibration solutions A (7.3) are within 1 °C of the same temperature.

7.4.1.6 Aspirate nitric acid diluted 1 + 19 and zero the instrument.

7.4.1.7 Aspirate the test solution(s) and note the reading to determine its place within the set of calibration solutions A.

7.4.1.8 Aspirate nitric acid diluted 1 + 19 until the initial reading is obtained. Zero the instrument if necessary.

7.4.1.9 Aspirate the set of calibration solutions A (7.3) and the test solution(s) in the order of increasing instrument response, starting with the zero member. When a stable response is obtained, record the reading. Flush the system by aspirating nitric acid diluted 1 + 19 between each test or calibration solution.

NOTE — Avoid aspirating solutions with a high concentration of nickel for long periods without flushing, otherwise the burner may tend to clog.

7.4.1.10 Repeat the measurement of the full set of the calibration and test solutions twice more and record the data.

7.4.2 Plotting of the calibration graphs

Plot the average instrument reading against the concentration of the analyte in the calibration solutions for each set of measurements. Proceed as directed in clause 9.

NOTES

1 In this method, any effect of non-specific absorption and light scatter is compensated for by matching the matrix of the calibration solutions with the test solutions. Also, since the same lot of nitric acid is used for both calibration and test solutions, the blank test is incorporated in the calibration graph. Thus, the calibration graph may not pass through the origin.

2 Some instruments may be adjusted to give a read-out directly in concentration of the analyte. A graph of instrument response versus concentration should be plotted to check the validity of the readings.

8 Procedure B

This procedure is applicable to 0,01 to 0,25 % (m/m) of cobalt, copper, iron and manganese and 0,005 to 0,025 % (m/m) of zinc.

8.1 Preparation of test solution

8.1.1 If a test solution has been prepared by procedure A (7.1), pipette a 100,0 ml aliquot portion into a 250 ml one-mark volumetric flask and dilute to the mark with nitric acid (4.3). Otherwise proceed as directed in 8.1.2.

8.1.2 Weigh, to the nearest 0,005 g, 1,9 to 2,1 g of the laboratory sample (6.2), transfer to a 400 ml beaker and dissolve in 20 ml of nitric acid (4.2). Complete the preparation as directed in 7.1.

8.2 Blank test

The zero member of the set of calibration solutions B (8.3) serves as the blank test (see 7.2).

8.3 Preparation of the set of calibration solutions B

8.3.1 This set corresponds to 0; 2,5; 5,0; 10,0; 15,0; 20,0; and 25,0 mg Co, Cu, Fe, and Mn per litre and 0; 0,25; 0,5; 1,0; 1,5; 2,0; and 2,5 mg of Zn per litre (see table 5). All the solutions contain a matrix of 10 g of Ni per litre.

Table 5 — Set of calibration solutions B

No.	Volume of mixed analyte standard solution B (4.4.3) (ml)	Analyte concentration (mg/l)	
		Co, Cu, Fe, Mn	Zn
1	0	0	0
2	5,0	2,5	0,25
3	10,0	5,0	0,5
4	20,0	10,0	1,0
5	30,0	15,0	1,5
6	40,0	20,0	2,0
7	50,0	25,0	2,5

8.3.2 Weigh, to the nearest 0,005 g, seven separate 2,00 g portions of nickel powder (4.1) and transfer to 400 ml beakers. Dissolve as directed in 8.1.2.

8.3.3 Add, using a burette, 0; 5,0; 10,0; 20,0; 30,0; 40,0; and 50,0 ml respectively of the mixed analyte standard solution B (4.4.3) to the 200 ml flasks. Make up to the mark with water and mix.

8.3.4 The solution with no analyte added is the zero member, which also serves as the blank test (see 8.2).

NOTE — For convenience a stock solution of 80 g of nickel nitrate per litre may be prepared by dissolving 20,0 g of nickel powder (4.1) in water and 120 ml of nitric acid (4.2) in an 800 ml beaker and filtering through glass-wool washed with nitric acid (4.2) or a cellulose filter into a 250 ml one-mark volumetric flask. Aliquots (25,0 ml) of this solution are then evaporated and processed as directed in 8.1.2 and 8.3.3.

8.4 Calibration and determination

8.4.1 Spectrometric measurements

8.4.1.1 The spectral lines specified in table 6 shall be used in the analysis.

Table 6 — Spectral lines — Procedure B

Element	Co	Cu	Fe	Mn	Zn
Wavelength (nm)	241,2	327,4	252,3	403,1	213,9

8.4.1.2 Proceed as directed in 7.4.1.3 and 7.4.1.4.

8.4.1.3 Proceed as directed in 7.4.1.5 to 7.4.1.10 inclusivesubstituting the set of calibration solutions B (8.3) for the set of calibration solutions A (7.3).

8.4.2 Preparation of the calibration graphs

See 7.4.2.

9 Expression of results

9.1 Procedure A

9.1.1 Determine the concentration of the analyte in the test solution from the corresponding calibration graphs (7.4.2) for each of the three sets of instrument readings recorded.

9.1.2 The analyte content, expressed as a percentage by mass, is given by the formula:

$$\frac{\varrho \times V}{m} \times 10^{-4}$$

where:

ϱ is the concentration, in milligrams per litre, of analyte found in the test solution;

V is the volume, in millilitres, of the test solution;

m is the mass, in grams, of the test portion.

NOTE — The average of the results from the three readings as calculated in 9.1.2 comprises a single determination. The three results give an indication of the precision of the atomic absorption measurements.

9.2 Procedure B

9.2.1 Determine the concentration of the analyte in the test solution from the corresponding calibration curves (8.4.2) for each of the three sets of instrument readings recorded.

9.2.2 For the procedure in 8.1.1, the analyte content, expressed as a percentage by mass, is given by the formula

$$\frac{\varrho \times V}{m} \times 2{,}5 \times 10^{-4}$$

where

ϱ, V and m have the same meaning as in 9.1.2;

2,5 is the correction factor for the dilution made.

9.2.3 For the procedure in 8.1.2, use the formula given in 9.1.2.

9.3 Precision

This International Standard was subjected to an inter-laboratory test programme involving 18 laboratories in nine countries. Twelve samples were analysed to cover the scope of the method. Of these, nine samples were specially prepared by melting and granulation, one by chemical precipitation, and two were commercial products.

A statistical report of interlaboratory tests is given in annex B.

It should be noted that the reproducibility data include errors due to any inhomogeneity of the test samples as well as variations due to change in analyst, instrument and laboratory. These data therefore represent the worst conditions.

For optimum repeatability and reproducibility the atomic absorption instrument shall meet the operating performance requirements specified in annex A.

10 Interferences and precautions

10.1 For the determination of silver, care shall be taken to avoid contamination of the sample and calibration solutions with chloride ion.

10.2 Elements ordinarily present in nickel do not interfere in the atomic absorption analysis.

10.3 The full range is covered by two sets of calibration solutions, one set in a 25 g/l nickel matrix for concentration levels up to 0,01 % (m/m) of the analyte [0,005 % (m/m) for Zn], and the second in a 10 g/l nickel matrix for 0,01 to 0,25 % (m/m) [0,005 % to 0,025 % (m/m) for Zn].

10.4 Potential background absorption interference is eliminated by use of matched matrix standards prepared from high purity nickel.

10.5 The purity of the nickel powder may be checked by measuring the specific and non-specific absorption of the matrix solution.

11 Special cases

11.1 High copper and cobalt

For test samples containing greater than 0,25 % (m/m) and less than 2 % (m/m) of cobalt or copper, further dilutions of the test solution with nitric acid (4.3) may be made. The nickel content of the calibration solutions should be matched with those of the test solutions.

11.2 Sample inhomogeneity

If some inhomogeneity is suspected in the laboratory sample, or if the pieces are relatively large, it is desirable to use a higher mass of sample to prepare the test solution. Under such circumstances a sample mass of 25 g in a final volume of 1 000 ml is recommended. The amount of nitric acid should be increased in proportion. Even larger sample masses can be used to prepare a more concentrated nickel test solution. However, this shall then be diluted to give a test portion containing 25 g of nickel per litre to match the calibration solutions.

12 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.

Annex A

Checking of spectrometer performance parameters

(This annex forms an integral part of the Standard.)

A.0 Introduction

The performance of atomic absorption spectrometers of the same or different manufacture may vary from instrument to instrument. It is therefore essential to establish that a particular instrument meets certain performance requirements before it is used in the methods specified in this International Standard.

A.1 Initial instrument adjustments

A.1.1 Set up the atomic absorption spectrometer to operate with an air-acetylene flame using a single slot (normally about 10 cm) laminar flow burner head according to the manufacturer's instructions.

A.1.2 Use a single element hollow cathode, single element electrode-less discharge or other appropriate single element lamp as the light source for the element under test. Operate the source as recommended by the instrument manufacturer.

NOTE — The use of multi-element lamps is not generally recommended although some binary alloy lamps give a more stable emission than single element lamps.

A.1.3 Light the burner and aspirate water until thermal equilibrium is reached. A fuel-lean flame shall be used in the methods specified in this International Standard.

A.1.4 Aspirate a mid-range calibration solution of the element under test and adjust the instrument to give optimum absorption. Use the wavelengths specified in this International Standard and the slit setting or bandpass recommended by the instrument manufacturer for the element under test. The use of scale expansion may be necessary.

A.1.5 Flush the burner system by aspirating nitric acid diluted 1 + 19 (4.3), adjust the instrument zero and proceed with the performance parameter check as directed in A.2.2 to A.2.4 inclusive.

NOTE — Avoid aspirating solutions with a high concentration of salts for long periods without flushing, otherwise the burner may tend to clog.

A.2 Instrument performance check

A.2.1 Performance check solutions

The calibration graph in this International Standard is normally established using seven calibration solutions including the zero member. For the instrument performance check, select two pairs of calibration solutions covering the upper and lower end of the calibration graph, such that the interval between the two calibration solutions of highest concentration is equal to that between the reference solution and the calibration solution of low concentration, i.e. use solutions 1, 3, 6 and 7 in table 2 or 5.

A.2.2 Readability

A.2.2.1 Aspirate the two calibration solutions of highest concentrations of the element under test, record the instrument readings and calculate the difference.

A.2.2.2 Divide the difference in the readings by 20. The readability of the instrument is acceptable if this result is not less than the smallest effective interval which can be read or estimated on the instrument read-out.

A.2.3 Linearity of instrument response

A.2.3.1 Aspirate the zero member solution and the calibration solution of low concentration of the element under test (A.2.1). Record the instrument readings and calculate the difference.

A.2.3.2 Divide the difference in the readings for the two calibration solutions of highest concentration as determined in A.2.2.1 by the difference between the zero member and calibration solution of low concentration.

A.2.3.3 The linearity of the instrument response is acceptable if this ratio is 0,70 or greater.

A.2.3.4 If the ratio is less than 0,70, further adjustments to the instrument may give acceptable results. Otherwise the operating range of the method shall be reduced by lowering the concentration of the calibration solution of highest concentration.

A.2.4 Minimum stability

A.2.4.1 Aspirate nitric acid (4.3) and zero the instrument.

A.2.4.2 Aspirate the calibration solution of highest concentration and record the reading.

A.2.4.3 Aspirate nitric acid (4.3).

NOTE — The instrument reading should return to zero.

A.2.4.4 Repeat the measurement of the calibration solution of highest concentration six times, aspirating nitric acid (4.3) between readings but not adjusting any instrumental settings.

A.2.4.5 The variability (VA), expressed as a percentage, of the readings of the calibration solution of highest concentration, is given by the formula

$$\frac{(A_h - A_l)\,0{,}40}{\bar{A}} \times 100$$

where

$\bar{A}$ is the average instrument reading for the calibration solution of highest concentration calculated from the six readings taken;

A_h is the highest of the six instrument readings;

A_l is the lowest of the six instrument readings.

NOTE — $(A_h - A_l)0{,}40$ is an estimate of the standard deviation.

A.2.4.6 The instrument meets the minimum stability requirements if the variability is less than 1,5 %.

NOTE — This test may, in addition, be applied to other points on the calibration graph. It may also be applied to evaluation of the minimum stability of the instrument zero.

Annex B

Statistical report of interlaboratory tests

(This annex is given for information only.)

B.0 Introduction

This International Standard was subjected to an interlaboratory test programme involving 18 laboratories in nine countries. Twelve samples of nickel metal were analysed to cover the full range of the scope of the method. Of these, 10 were specially prepared as materials containing the impurity levels covered were not available commercially. The test programme was designed to determine within- and between-laboratory reproducibility of the method in the spirit of ISO 5725.

B.1 References

ISO 3534, *Statistics — Vocabulary and symbols.*

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

B.2 Definitions

In this annex, the definitions of ISO 3534 apply with the following modification. The repeatability has to be substituted by "within-laboratory reproducibility" due to the fact that changes of analyst and/or instruments have taken place within each laboratory. The within-laboratory reproducibility includes the repeatability and the effect of the factor of changing analyst or apparatus.

B.3 Design of test programme

B.3.1 The test programme was designed to include, in a single laboratory, variations due to a difference of operator and/or atomic absorption instrument while maintaining the test solution constant. Two weighings from each sample were therefore analysed by the same analyst using two instruments or by a second analyst using the same instrument.

B.3.2 Test samples were selected such that the lower end of the concentration range of the scope of the method could be determined.

B.4 Test samples

B.4.1 Nine test samples were specially prepared by melting high purity nickel, adding trace elements and granulating the product by atomization in water. Conditions were selected to give a fairly coarse product to simulate fine drilling or millings of metal.

B.4.2 Various size fractions of each of the nine samples were analysed to check the homogeneity. Unfortunately six (the P series) had been unavoidably contaminated with copper which was inhomogeneously distributed. The minus 28 plus 65 Tyler screen (minus 0,60 mm plus 0,21 mm) fraction was taken from each to provide uniform test samples. The minus 14 plus 48 Tyler screen (minus 1,2 mm plus 0,3 mm) fraction was taken from the other three specially prepared samples (the J series) covering the higher ranges of concentration.

B.4.3 One sample was prepared by chemical precipitation to test higher levels of cobalt and copper.

B.4.4 The remaining two test samples were a commercial nickel powder and millings from a wrought nickel bar. A commercial high purity nickel powder was provided to each laboratory for preparation of standards.

B.5 Statistical procedures

B.5.1 Computer program

A computer program was used to perform statistical analysis in the spirit of ISO 5725. The program computes the mean, the within- and between-laboratory standard deviations and the corresponding reproducibilities. Various statistical tests were performed to identify outliers which were rejected.

B.5.2 Statistical tests for outliers

The Cochran and Dixon tests were applied independently to the data at the 95 % confidence level according to ISO 5725. The principle of the Cochran test is that a set of results is an outlier if the within-analyst or within-laboratory variance is too large in relation to others. Dixon's test is to determine if the mean from an analyst or laboratory is too far from other means.

B.5.3 Calculation of variances and reproducibilities

The pairs of results from each of two analysts (or instruments) for each laboratory completing the test programme were treated according to ISO 5725 to give the within-laboratory variance and a between-laboratory variance. The corresponding reproducibilities were calculated.

The following information was thus obtained:

s_w^2 within-laboratory variance;

s_b^2 between-laboratory variance;

R_w reproducibility, within laboratory (including a change in analyst or instrument)

$$R_w = 2{,}83\sqrt{s_w^2}$$

R reproducibility, between laboratories

$$R = 2{,}83\sqrt{s_w^2 + s_b^2}$$

B.6 Results of statistical analysis

B.6.1 The results of the statistical analysis for each element covered by the scope of this International Standard are given in table 7 for procedure A and table 8 for procedure B.

B.6.2 In evaluating these results it should be borne in mind that the test samples were prepared in the laboratory and may not be as homogeneous as commercial production. Also, the calibration procedure was modified as a result of the test programme so that a separate calibration is used for each set of measurements. This is expected to improve the agreement between individual results.

B.6.3 Results for elements which were outside the scope of the method are given for information. Also some laboratories did not complete the full test programme on all samples which limited the amount of data which could be used for this statistical report.

Table 7 — Results of statistical analysis — Procedure A

Sample reference	No. of laboratories	Results accepted (%)	Mean (g/t)	Within-laboratory standard deviation, s_w	Between-laboratory standard deviation, s_b	Within-laboratory repro-ducibility, R_w	Between-laboratory repro-ducibility, R
Silver							
P45	10	100	4,3	0,12	0,42	0,3	1,2
P44	15	80	7,7	0,17	0,18	0,5	0,7
P46	16	94	9,5	0,41	0,31	1,16	1,5
P41	12	83	19,1	0,30	0,53	0,8	1,7
J63	4	100	23,2	0,37	0,69	1,0	2,2
P43	12	92	28,3	0,59	0,49	1,7	2,2
J61	16	75	97,0	0,89	4,94	2,5	14,2
Bismuth							
P45[1]	9	89	8,6	1,15	0,81	3,2	4,0
P46[1]	10	100	9,9	1,20	2,49	3,4	7,8
P44	10	90	13,3	0,95	2,52	2,7	7,6
P41	10	80	17,1	0,98	1,35	2,8	4,7
P43	10	90	24,5	1,09	1,34	3,1	4,9
J61	11	91	103,7	1,55	1,29	4,4	5,7
Cadmium							
P46	11	100	1,9	0,10	0,27	0,3	0,8
J63	4	75	2,5	0,06	0,30	0,2	0,9
J61	15	93	13,5	0,26	0,85	0,7	2,5
S65	12	100	22,5	0,23	0,87	0,7	2,5
Cobalt							
P46[1]	15	87	3,2	0,16	1,10	0,5	3,1
P45[1]	11	82	5,5	0,62	0,39	1,8	2,1
P43	12	83	10,5	0,26	0,52	0,7	1,6
P44	15	87	15,5	0,26	1,37	0,7	4,0
P41	12	83	18,5	0,38	0,34	1,1	1,4
J62	16	81	50,8	0,80	0,71	2,3	3,0
J61	13	100	100,2	1,34	1,64	3,8	6,0
Copper[2]							
S65	12	100	7,9	0,41	0,65	1,2	2,2
J62	16	100	51,7	0,32	0,82	0,9	2,5
J61	15	87	100,6	0,32	1,40	0,9	4,1
Iron							
P46	15	80	24,1	0,70	1,94	2,0	5,9
P45	11	72	29,8	1,16	1,78	3,3	6,0
P44	14	78	31,1	0,45	2,01	1,3	5,8
P41	12	83	43,7	0,64	3,57	1,8	10,3
S65	11	82	47,4	0,91	1,82	2,6	5,8
Manganese							
P44[1]	13	85	3,3	0,14	0,39	0,4	1,2
P41	11	82	5,4	0,12	0,69	0,3	2,0
P46	16	94	7,0	0,16	0,69	0,5	2,0
P45	11	100	10,7	0,30	0,63	0,8	2,0
P43	11	91	20,0	0,18	0,47	0,5	1,4
J62	16	100	53,6	0,45	1,21	1,3	3,7
J61	12	92	102,8	0,97	1,57	2,7	5,2
Lead							
P45[1]	10	100	3,9	0,64	0,68	1,8	2,7
H79	6	83	7,8	0,12	0,58	0,3	1,7
P46	12	92	9,0	1,07	0,67	3,0	3,6
P41	11	100	20,2	1,13	1,25	3,2	4,8
P44	12	92	25,2	0,84	0,35	2,4	2,6
J62	14	93	35,0	0,38	1,38	1,1	4,1
J63	4	100	36,5	0,61	0,00	1,7	1,7
J61	14	79	77,7	0,69	1,47	2,0	4,6
Zinc							
H79	6	100	2,9	0,14	0,52	0,4	1,5
P44	10	80	4,1	0,15	0,69	0,4	2,0
P41	11	91	5,0	0,25	0,52	0,7	1,6
P46	13	100	6,2	0,27	0,24	0,8	1,0
S65	12	83	10,1	0,33	0,52	0,9	1,7
P43	12	100	11,7	0,33	0,93	0,9	2,8
P45	10	100	12,8	0,81	1,16	2,3	4,0
J62	13	100	26,9	0,51	0,67	1,4	2,4

1) Below scope of method, included for information only.

2) Results for copper in the P series are not reported as the samples were not homogeneous with respect to copper.