INTERNATIONAL STANDARD

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Zinc sulfide concentrates — Determination of gold content — Acid dissolution/solvent extraction/flame atomic absorption spectrometric method

Concentrés sulfurés de zinc — Dosage de l'or — Méthode par dissolution acide, extraction à l'aide d'un solvant et spectrométrie d'absorption atomique dans la flamme

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Contents

International Organization for Standardization
Case postale 56 • CH-1211 Genève 20 • Switzerland
Internet iso@iso.ch

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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. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

International Standard ISO 15249 was prepared by Technical Commitee ISO/TC 183, *Copper, lead and zinc ores.*

Annexes A and B form an integral part of this International Standard. Annexes C and D are for information only.

Zinc sulfide concentrates — Determination of gold content — Acid dissolution/solvent extraction/flame atomic absorption spectrometric method

1 Scope

This International Standard specifies an acid decomposition, solvent extraction, flame atomic absorption spectrometric procedure for the determination of gold in zinc sulfide concentrates.

The method is applicable to the determination of gold in zinc concentrates containing up to 60 % (*m/m*) zinc in the form of zinc blende and related materials.

The method is applicable to gold contents from 0,5 g/t to 12 g/t.

2 Normative references

The following standards contain provisions which, through reference in this text, constitute provisions of this International Standard. At the time of publication, the editions indicated were valid. All standards are subject to revision, and parties to agreements based on this International Standard are encouraged to investigate the possibility of applying the most recent editions of the standards indicated below. Members of IEC and ISO maintain registers of currently valid International Standards.

ISO 385-1:1984, *Laboratory glassware — Burettes — Part 1: General requirements.*

ISO 648:1977, *Laboratory glassware — One-mark pipettes.*

ISO 1042:1998, *Laboratory glassware — One-mark volumetric flasks.*

ISO 3696:1987, *Water for analytical laboratory use — Specification and test methods*.

ISO 4787:1984, *Laboratory glassware — Volumetric glassware — Methods for use and testing of capacity*.

ISO 9599:1991, *Copper, lead and zinc sulfide concentrates — Determination of hygroscopic moisture in the analysis sample — Gravimetric method*.

3 Principle

Roasting of the concentrate at 450 °C and 600 °C to remove arsenic and sulfur, followed by decomposition in bromine-aqua regia-hydrofluoric acid. Extraction of the gold into DIBK containing Aliquat 336 from an aqua regia medium and determination by flame atomic absorption spectrometric at 242,8 nm.

4 Reagents

During the analysis, use only reagents of recognized analytical grade and water that complies with grade 2 of ISO 3696.

4.1 Gold metal, minimum 99,99 % purity.

4.2 Nitric acid, (ρ_{20} 1,42 g/ml).

4.3 Hydrochloric acid, (ρ_{20} 1,16 g/ml to 1,19 g/ml).

4.4 Aqua regia

Mix three parts hydrochloric acid (4.3) and one part nitric acid (4.2) with three parts of water. Prepare freshly as required.

4.5 Bromine liquid, 99,5 % *m/m*.

4.6 Hydrofluoric acid (ρ_{20} 1,19 g/ml).

WARNING — Even when diluted, hydrofluoric acid is extremely dangerous and harmful to the eyes and skin: rubber gloves and goggles should be worn when using this acid. Hydrofluoric acid attacks glassware. Care should be taken to minimize the time of acid contact with glassware. Use only in a mechanically ventilated fume cupboard.

4.7 Di-iso butyl ketone (ρ_{20} 0,81 g/ml).

4.8 Aliquat 336 (methyl-trioctyl ammonium chloride).

4.9 1 % Aliquat 336 in di-iso butyl ketone

Add 1 ml of Aliquat 336 (4.8) to 99 ml of di-iso butyl ketone (4.7) and mix thoroughly.

4.10 Gold standard solutions

NOTE Standard solutions should be prepared at the same ambient temperature as that at which the determinations are to be conducted.

4.10.1 Gold standard solution (1 000 µg/ml).

Weigh 0,100 0 g of gold metal (4.1) into a 50 ml beaker, add 10 ml aqua regia (4.4), cover and heat to dissolve the gold. Wash and remove the cover, and evaporate to near dryness (do not allow to go to dryness otherwise gold will precipitate). Cool, add 5 ml of hydrochloric acid (4.3) and transfer the solution quantitatively to a 100 ml volumetric flask, dilute to volume with water and mix thoroughly.

4.10.2 Gold standard solution (100 µg/ml).

Pipette 10 ml of gold standard solution (4.10.1) into a 100 ml volumetric flask, add 5 ml of hydrochloric acid (4.3), dilute to volume with water and mix thoroughly.

4.10.3 Gold standard solution (10 µg/ml).

Pipette 10 ml of gold standard solution (4.10.2) into a 100 ml volumetric flask, add 5 ml of hydrochloric acid (4.3), dilute to volume with water and mix thoroughly.

This solution shall be freshly prepared.

4.11 Calibration solutions

NOTE Calibration solutions should be prepared at the same ambient temperature as that at which the determinations are to be conducted.

To each of seven 125 ml separating funnels add 75 ml of water and 20 ml of aqua regia (4.4). Add from a burette (5.2) 0 ml, 1 ml, 2 ml, 3 ml, 4 ml, 5 ml and 6 ml of gold standard solution (4.10.3). Treat these solutions using the extraction procedure given in 7.4.

These standards contain 0 µg, 10 µg, 20 µg, 30 µg, 40 µg, 50 µg and 60 µg of gold.

5 Apparatus

Ordinary laboratory equipment plus the following.

5.1 Volumetric glassware, of class A complying with ISO 385-1, ISO 648 and ISO 1042 and used in accordance with ISO 4787.

5.2 Burette, A grade, 10 ml capacity capable of being read to 0,02 ml.

5.3 Muffle furnace, capable of giving an adequate zone of uniform temperature between 450 °C and 600 °C. A ventilated furnace is preferred.

5.4 Crucibles, porcelain, having a depth of 10 mm to 15 mm and a diameter of 60 mm to 75 mm.

5.5 Atomic absorption spectrometer (AAS), equipped with background correction and a glass bead, rather than a flow spoiler, in the spray chamber. Scale expansion and a flow adjustable nebulizer are recommended.

5.6 Centrifuge, capable of holding at least 15 ml tubes and revolving at 0,833 s^{-1} (3 000 rpm).

5.7 Centrifuge tubes, 15 ml volume with caps. Polypropylene is suitable.

5.8 Separating funnels, of 125 ml capacity. Borosilicate glass with PTFE stopcocks are recommended.

6 Sample

6.1 Test sample

Prepare an air-equilibrated test sample in accordance with ISO 9599.

NOTE A test sample is not required if predried test portions are to be used (see annex A).

6.2 Test portion

Taking multiple increments, extract a test portion from the test sample in such a manner that it is representative of the whole contents of the dish or tray. Weigh, to the nearest 0,1 mg, approximately 5 g of the test sample. At the same time as the test portion is weighed, weigh test portions for the level of hygroscopic moisture in accordance with ISO 9599.

Alternatively, the method specified in annex A may be used to prepare predried test portions directly from the laboratory sample.

7 Procedure

7.1 Number of determinations

Carry out the determinations at least in duplicate, and as far as possible under repeatability conditions, on each test sample.

NOTE Repeatability conditions exist where mutually independent test results are obtained with the same method on identical test material in the same laboratory by the same operator using the same equipment within short intervals of time.

7.2 Blank test

Carry out a blank test in parallel with the analysis using all reagents specified in the determination but omitting the test portion. The purpose of the blank test in this method is to check the quality of the reagents. If a significant blank value is obtained as a result of the blank test, check all reagents and rectify the problem.

7.3 Decomposition of test portion

Transfer the test portion to a porcelain crucible and place in the muffle furnace (5.3) at 450 °C and heat for 2 h. Raise the muffle furnace temperature to 600 °C and continue heating for 1 h.

Remove the crucible from the furnace, cool, and transfer the roasted test portion to a 250 ml conical beaker.

Add 10 ml of water, swirl to form a slurry and add 2 ml of bromine (4.5) and mix. Cover with a watchglass, swirl to mix and allow to stand at room temperature for 15 min.

Add 15 ml of hydrochloric acid (4.3) and digest on a hotplate at 90 °C until fumes of bromine are expelled. Continue the digestion for 30 min. Remove from the hotplate and cool.

Remove the watchglass and rinse the underside with a minimum of water, collecting the washings in the conical beaker. Carefully add 10 ml of nitric acid (4.2) and 1 ml of hydrofluoric acid (4.6). Return the beaker to the hotplate and gently evaporate to near dryness.

NOTE Do not allow the digestion mixture to go to dryness, as gold will be lost.

Rinse the sides of the beaker with a minimum of water, add 20 ml of aqua regia (4.4), cover with the watchglass, return to the hotplate and heat gently for 10 min. Remove from the hotplate and cool.

7.4 Extraction

Transfer the test solution to a 125 ml separating funnel (5.8), add sufficient water to make the volume to 100 ml and swirl to mix.

Add 8 ml of 1 % Aliquat in di-iso butyl ketone (4.9), stopper and shake for 1 min. Allow the phases to separate and slowly run off the lower aqueous layer until about 4 ml of aqueous material remain. Transfer these, with the organic layer, to a 15 ml centrifuge tube (5.7). Centrifuge until a clear organic layer is obtained.

7.5 Determination of gold

Determine the gold content in the organic layer by flame atomic absorption spectrometry using calibration solutions (4.11). As a guide, the following atomic absorption conditions are recommended; however, the instrument should be optimized to give maximum sensitivity and as near as practical to a linear relationship between absorbance and concentration.

- flame: air-acetylene oxidizing
- wavelength: 242,8 nm
- lamp current: 4 mA
- background corrector: on
- aspiration rate: aspirate di-iso butyl ketone as waste solution; adjust (reduce) flow rate to give an oxidizing flame
- integration time: 3 s
- number of integrations: 5

NOTE The organic used for extraction, [di-iso butyl ketone (4.7)] should be aspirated between each standard solution and between each test solution during the determination.

Perform three measurements on each standard solution. Calculate to three significant figures the mean absorbance for each standard solution, provided that the range of values does not exceed 0,003 absorbance units. If this range is exceeded, repeat the calibrations.

The test solutions should be treated in the same manner. Plot a calibration graph of absorbance versus concentration of gold in the organic layer.

8 Expression of results

The gold content of the test portion w_{Au}, expressed in grams per tonne, is given by the following equation:

$$w_{\mathrm{Au}} = \frac{C}{m} \times \frac{100}{100 - H} \qquad \text{. . . (1)}$$

where

C is the gold content of the organic layer in micrograms;

m is the mass of test portion in grams;

H is the hygroscopic moisture content as a percentage of the test portion (in the case of a predried test portion being used, $H = 0$).

9 Precision

9.1 Expression of precision

The precision of this analytical method is expressed by the following equations:

$$s_{\mathrm{r}} = 0{,}037\,2\ \overline{X} + 0{,}004\,2 \qquad \text{. . . (2)}$$

$$s_{\mathrm{L}} = 0{,}082\,2\ \overline{X} + 0{,}100\,2 \qquad \text{. . . (3)}$$

where

$\overline{X}$ is the mean content of gold, in grams per tonne, in the sample;

s_{r} is the within-laboratory standard deviation, in grams of gold per tonne;

s_{L} is the between-laboratories standard deviation, in grams of gold per tonne.

See annex C.

9.2 Method for obtaining the final result

See annex B.

Calculate the following quantities from the duplicate results X_1 and X_2 and process according to the flow chart in annex B:

Mean of duplicates $\overline{X} = (X_1 + X_2)/2$ . . . (4)

Within-laboratory standard deviation $s_{\mathrm{r}} = 0{,}037\,2\ \overline{X} + 0{,}004\,2$ . . . (5)

Repeatability limit $r = 2{,}8\ s_{\mathrm{r}}$ . . . (6)

9.3 Precision between laboratories

The precision between laboratories is used to determine the agreement between the results reported by two (or more) laboratories. It is assumed that all laboratories have followed the same procedure.

Calculate the following quantities.

Mean of final results $\mu_{1,2} = (\mu_1 + \mu_2)/2$ . . . (7)

Between-laboratories standard deviation $s_L = 0{,}082\,2\ \mu_{1,2} + 0{,}100\,2$ . . . (8)

Within-laboratory standard deviation $s_r = 0{,}037\,2\ \mu_{1,2} + 0{,}004\,2$ . . . (9)

Permissible difference $P = 2{,}8\sqrt{(s_L^2 + s_r^2/2)}$ . . . (10)

Range $E = |\mu_1 - \mu_2|$ . . . (11)

where

μ_1 is the final result, in grams of gold per tonne, reported by laboratory 1;

μ_2 is the final result, in grams of gold per tonne, reported by laboratory 2.

If E is equal to or less than P, the final results are in agreement.

9.4 Check of trueness

The trueness of the analytical method can be checked by applying it to a certified reference material (CRM). The procedure is the same as that described in clause 7. When the precision has been confirmed, the final laboratory result can be compared with the certified value, A_c.

The following two possibilities exist:

$$\left| \mu_c - A_c \right| \leqslant C \qquad . . . (12)$$

If this condition exists, the difference between the reported result and the certified value is statistically insignificant.

$$\left| \mu_c - A_c \right| > C \qquad . . . (13)$$

If this condition exists, the difference between the reported result and the certified value is statistically significant.

In equations (12) and (13), the symbols are defined as follows:

μ_c is the final result, in grams of gold per tonne, of the certified reference material;

A_c is the certified value, in grams of gold per tonne, of the certified reference material;

C is a quantity, in grams of gold per tonne, depending on the type of the certified reference material used.

NOTE 1 The reference materials used for this purpose should be prepared and certified in accordance with ISO Guide 35.

Where the reference material is certified/characterized by an interlaboratory test programme, the quantity C, in grams of gold per tonne, is given by the following equation:

$$C = 2\sqrt{s_L^2 + \left(s_r^2/n\right) + s^2\{A_c\}} \qquad . . . (14)$$

where

$s^2\{A_c\}$ is the variance of the certified value;

n is the number of replicate determinations.

Where the reference material is certified/characterized by one laboratory, the quantity C, in grams of gold per tonne, is given by the following equation:

$$C = 2\sqrt{2s_L^2 + \left(s_r^2/n\right)} \qquad \text{. . . (15)}$$

NOTE 2 It is recommended that this type of certified reference material be avoided, unless the particular CRM is known to have an unbiased certified value.

10 Test report

The test report shall contain the following information:

a) identification of the test sample;

b) reference to this International Standard, i.e. ISO 15249;

c) gold content of the sample, expressed in grams per tonne;

d) date on which the test was carried out;

e) any occurrence noticed during the determination that may have had an influence on the results.

Annex A
(normative)

Procedure for the preparation and determination of the mass of a predried test portion

A.1 Scope

This procedure sets out a method for the preparation and determination of the mass of a predried test portion in the analysis of zinc sulfide concentrates. The method is applicable to zinc sulfide concentrates not susceptible to oxidation and having hygroscopic moisture contents ranging from 0,05 % to 2 %.

A.2 Principle

The test portion to be used for analysis is dried in air in an oven maintained at 105 °C ± 5 °C. The dried test portion is then weighed and used for the analysis. No correction for moisture is required.

A.3 Reagents

A.3.1 Desiccant, such as self-indicating silica gel or anhydrous magnesium perchlorate.

WARNING — Care should be taken when disposing of exhausted magnesium perchlorate. It should be washed down the sink with a stream of running water.

A.4 Apparatus

Ordinary laboratory equipment and

A.4.1 Analytical balance, sensitive to 0,1 mg.

A.4.2 Weighing vessels, of glass or silica or corrosion-resistant metal having externally-fitting air-tight covers. For small test portions (less than 3 g), the mass of the vessel should be as small as possible, i.e. less than 20 g.

A.4.3 Laboratory oven, capable of maintaining a temperature of 105 °C ± 5 °C.

A.5 Procedure

A.5.1 Preparation of the weighing vessel

Dry the weighing vessel and vessel cover (A.4.2) by heating in a laboratory oven (A.4.3) at 105 °C ± 5 °C for 1 h. Transfer the vessel and vessel cover to a desiccator containing suitable fresh desiccant (A.3.1) and allow to cool to ambient temperature.

A.5.2 Test portion

Tare the dried weighing vessel and vessel cover. Immediately add a proportion of the laboratory sample to provide a suitable predried test portion. An accurate total mass of the test portion and weighing vessel is not required at this point.

A.5.3 Determination of the test portion dry mass

Transfer the uncovered weighing vessel and test portion and vessel cover to the laboratory oven (A.4.3) and dry at 105 °C ± 5 °C for 2 h. After the 2 h period, remove the weighing vessel and dry test portion from the oven, replace the vessel cover and allow to cool to ambient temperature in the desiccator. When cool, remove the weighing vessel and dry test portion and vessel cover from the desiccator and weigh to the nearest 0,1 mg (m_1) after slightly lifting the cover and quickly replacing it. Transfer the test portion to the appropriate analytical apparatus and immediately re-weigh the empty weighing vessel and vessel cover. Record the mass (m_2) to the nearest 0,1 mg.

NOTE For new concentrates of unknown characteristics, it is advisable to repeat the drying for another 2 h at 105 °C ± 5 °C and to re-weigh the weighing vessel and test portion plus vessel cover to the nearest 0,1 mg (m'_1). The mass of the test portion can be considered to be constant if the difference between m_1 and m'_1 is less than or equal to 0,5 mg. If this condition is not achieved, the drying and weighing steps should be repeated.

A.6 Calculation of the test portion dry mass

The dry mass of the test portion m_3, in grams, is given by the following equation:

$$m_3 = m_1 - m_2 \qquad \text{. . . (A.1)}$$

where

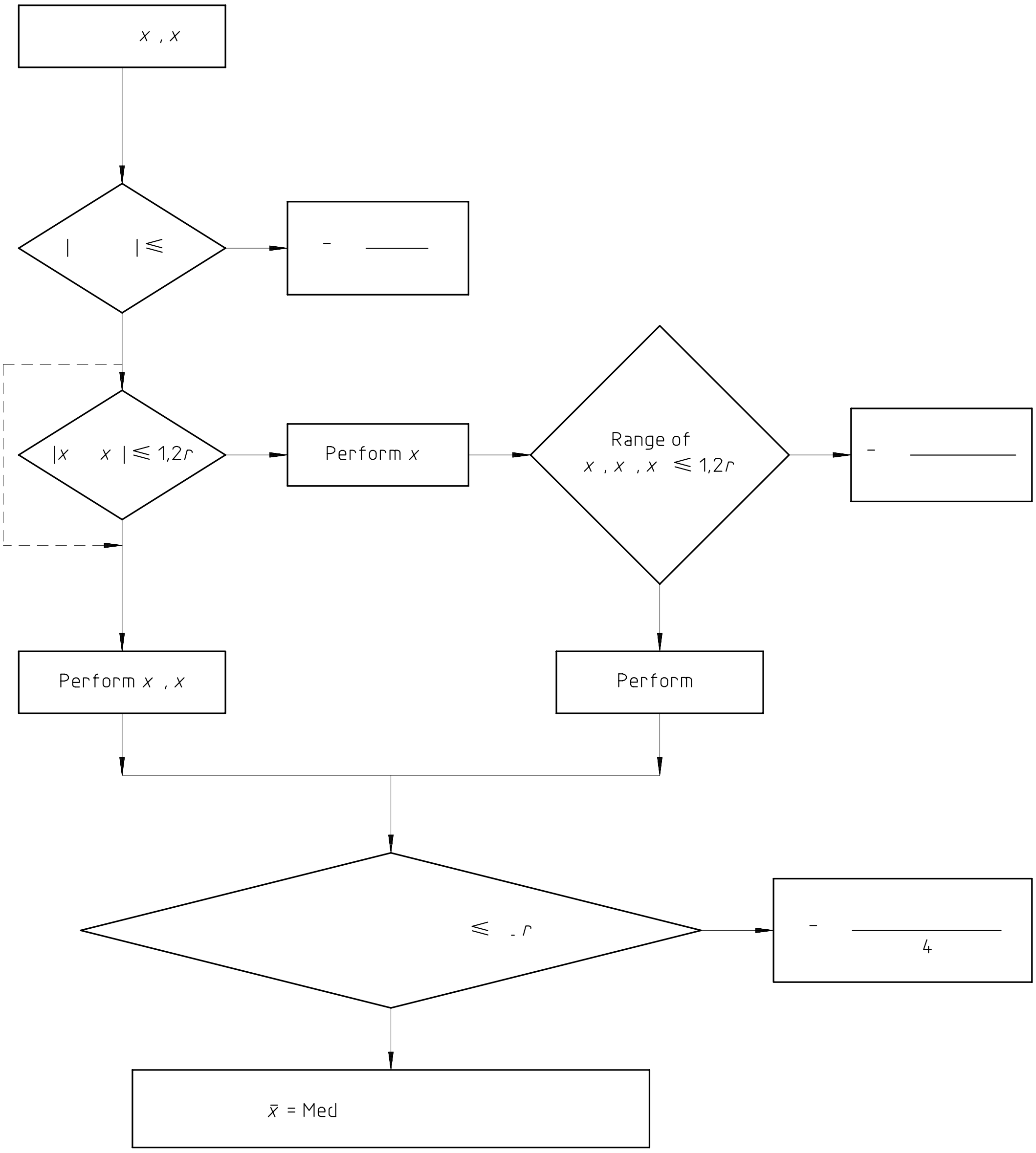
m_1 is the mass, in grams, of the dried test portion plus weighing vessel and its cover;

m_2 is the mass, in grams, of the empty weighing vessel plus its cover.

The mass of the dry test portion is the mass to be used to calculate the element content in the laboratory sample on a dry basis. No correction for hygroscopic moisture is required.

Annex B
(normative)

Flowsheet of the procedure for the acceptance of analytical values for test samples



r: defined in 9.2

Annex C
(informative)

Derivation of precision equations

C.1 Introduction

This International Standard was tested in an interlaboratory test programme involving eight countries and fifteen laboratories. Five samples of zinc concentrate covering the range up to 60 % (*m/m*) were analysed to determine the gold content. The test programme was designed to determine the repeatability and within-laboratory and between-laboratories reproducibilities in general, using the principles of ISO 5725.

C.2 Design of test programme

The analytical test programme was designed with the aim of providing maximum information. Each laboratory used two samples (two bags) of each concentrate and each sample was independently analysed twice.

C.3 Test samples

This test programme used five samples of zinc concentrate. The composition of these samples is shown in table C.1.

C.4 Statistical evaluation

The procedure for statistical evaluation is illustrated schematically in figure C.1. The results of the statistical evaluation are summarized in table C.2.

The estimated precisions (s_r, s_L, r and P) are plotted against their corresponding sample means on a graph as shown in figure C.2 and the regression equations of these precisions against sample means were computed and are presented in table C.2.

Table C.1 — Composition of zinc concentrate samples

Element	**Sample numbers**				
	89/1[1)]	**89/2**[1)]	**89/3**[1)]	**91/16**	**93/1**[2)]
Cu % (*m*/*m*)	0,61	0,34	0,22	0,53	0,23
Pb % (*m*/*m*)	3,50	3,01	5,54	3,72	3,24
Zn % (*m*/*m*)	47,14	53,69	50,15	46,76	46,68
Au g/t	10	3	0,5	7	2
Ag g/t	300	130	340	19	15
S % (*m*/*m*)	31,25	31,44	26,68	30,28	26,51
Fe % (*m*/*m*)	8,83	5,09	5,18	10,51	6,70
SiO_2 % (*m*/*m*)	3,42	4,35	7,33	3,78	12,74
Al_2O_3 % (*m*/*m*)	0,73	0,31	0,46	0,42	1,20
CaO % (*m*/*m*)	0,78	0,86	0,78	0,60	0,72
K_2O % (*m*/*m*)	0,32	0,16	0,16	0,22	0,31
MnO % (*m*/*m*)	0,55	0,64	0,30	0,14	0,15

1) Cominco (Canada).

2) Peak (Australia).

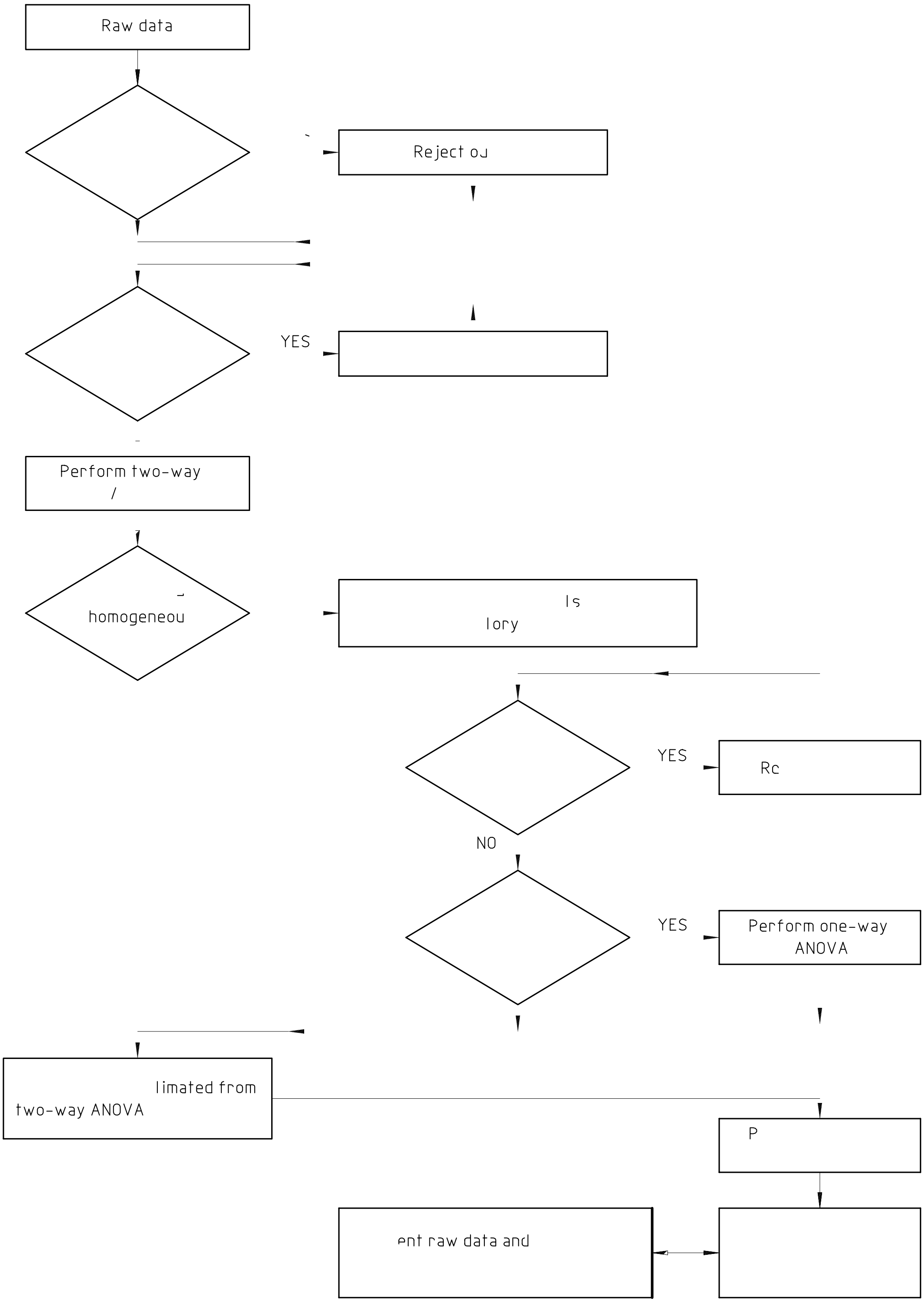


Figure C.1 — Flowsheet of procedure for statistical evaluation of analytical data resulting from international tests

Table C.2 — Summary of precisions for all samples — Gold

Sample number (see table C.1)	k_o	k	N_o	N	$\overline{\overline{X}}$	r	P	s_r	s_L	s_L/s_r
89-1	14	12	52	44	10,360	1,3099	2,5537	0,4628	0,9024	1,95
89-2	14	13	51	47	2,695	0,2689	0,7174	0,0950	0,2535	2,67
89-3	14	14	52	52	0,493	0,1233	0,3218	0,0436	0,1137	2,61
91-16	14	11	52	42	6,663	0,3715	2,1048	0,1313	0,7437	5,66
93-1	14	14	51	51	1,562	0,2758	0,7883	0,0975	0,2785	2,86

The regression equations are	Correlation coefficient
$r = 0{,}105\,2\ \overline{X} + 0{,}011\,9$	0,900
$P = 0{,}232\,7\ \overline{X} + 2{,}283\,7$	0,979
$s_r = 0{,}037\,2\ \overline{X} + 0{,}004\,2$	0,900
$s_L = 0{,}082\,2\ \overline{X} + 0{,}100\,2$	0,979

k_o is the total number of participating laboratories
k is the number of participating laboratories used for computation of precision
n_o is the total number of analytical results
n is the number of analytical results used for computation of precision
$\overline{\overline{X}}$ is the overall mean of the gold content, in grams per tonne
r is the permissible within-laboratory tolerance (repeatability), in grams of gold per tonne
P is the permissible between-laboratories tolerance, in grams of gold per tonne
s_r is the within-laboratory standard deviation, in grams of gold per tonne
s_L is the between-laboratories standard deviation, in grams of gold per tonne
$\overline{X}$ is the mean content of gold, in grams per tonne of the sample

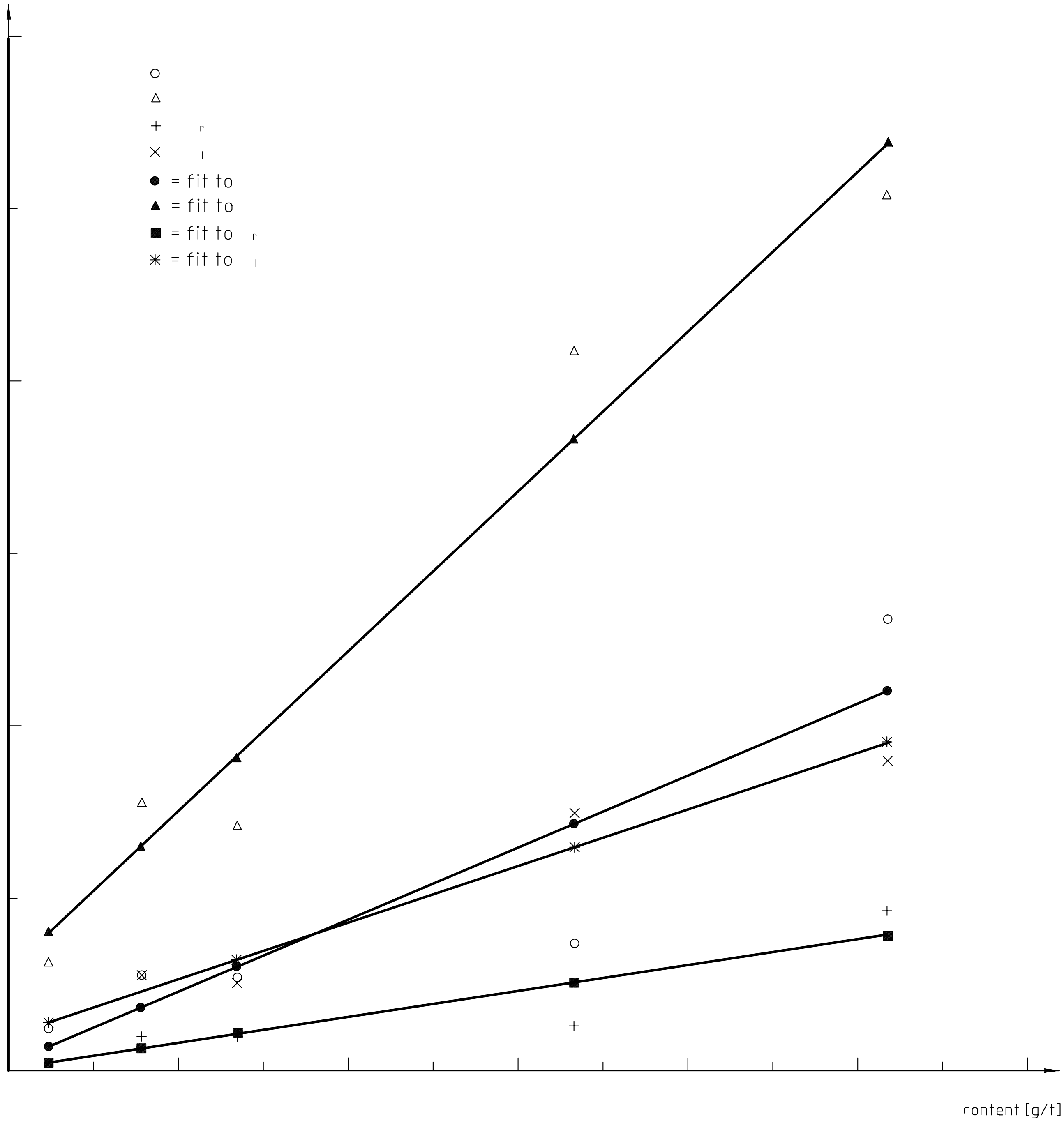


Figure C.2 — Least-squares fit of precision against the mean gold content

Annex D
(informative)

Bibliography

[1] ISO 5725:1986, *Precision of test methods — Determination of repeatability and reproducibility for a standard test method by inter-laboratory tests*.

[2] ISO Guide 35:1989, *Certification of reference materials — General and statistical principles*.

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