International Standard

ISO 5666/2

Water quality — Determination of total mercury by flameless atomic absorption spectrometry — Part 2 : Method after pretreatment with ultraviolet radiation

Qualité de l'eau — Dosage du mercure total par spectrométrie d'absorption atomique sans flamme — Partie 2 : Méthode après minéralisation par irradiation aux rayons ultraviolets

First edition — 1983-07-01

Price based on 8 pages

ISO 5666/2-1983 (E)

Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of developing International Standards is carried out through ISO technical committees. Every member body interested in a subject for which a technical committee has been authorized 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.

International Standard ISO 5666/2 was developed by Technical Committee ISO/TC 147, *Water quality*, and was circulated to the member bodies in December 1981.

It has been approved by the member bodies of the following countries :

Australia	Germany, F.R.	Romania
Belgium	Hungary	South Africa, Rep. of
Brazil	India	Spain
Canada	Italy	Sweden
Chile	Mexico	Switzerland
Czechoslovakia	Netherlands	United Kingdom
Egypt, Arab Rep. of	New Zealand	USSR
France	Poland	

The member body of the following country expressed disapproval of the document on technical grounds :

Japan

Water quality — Determination of total mercury by flameless atomic absorption spectrometry — Part 2 : Method after pretreatment with ultraviolet radiation

0 Introduction

This document constitutes the second part of an International Standard specifying methods for the determination of total mercury in water by flameless atomic absorption spectrometry.

Since various types of water may be tested for the presence of mercury, it has been considered preferable to standardize several methods of determination, which, although they are all based on the same instrumental technique (atomic absorption spectrometry), involve, nevertheless, sufficiently important procedural differences so that their respective fields of application differ significantly.

Thus, this part (part 2) specifies a method of determination after pretreatment with ultraviolet radiation and is applicable to drinking water and to water used for food and drink processing.

Part 1 specifies a method of determination after digestion with permanganate-peroxodisulfate and is applicable, in particular, to surface waters and domestic and industrial wastewaters.

Part 3, at present under study, will specify a method of determination after digestion with bromine and will apply to soft waters and brines, to drinking water and to other types of water containing only small amounts of organic matter.

Each of the three parts describes the method in its entirety and can therefore be used independently of the others.

1 Scope and field of application

This part of ISO 5666 specifies a flameless atomic absorption spectrometric method for the determination of total mercury in drinking water and in water used for food and drink processing.

The method permits determination of as little as 0,02 µg of mercury in the test portion used for the analysis. For a test portion of volume 100 ml, the lower limit of determination is 0,2 µg/l.

2 Reference

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

3 Principle

Pretreatment of a test portion by exposure to ultraviolet radiation for a period of 10 min, in order to decompose organic matter and organic mercury compounds and to convert all the mercury present to mercury(II).

Reduction of mercury(II) to metallic mercury by tin(II) chloride.

Entrainment of the mercury in a current of gas and determination of the mercury, as the monatomic vapour, by flameless atomic absorption spectrometry at a wavelength of 253,7 nm.

4 Reagents

During the analysis, use only the water (4.1) and reagents of recognized analytical quality, the mercury contents of which are as low as possible[1].

4.1 Demineralized-distilled water, or water of equivalent quality, free from mercury.

4.2 Sulfuric acid, $\varrho_{20} = 1,84$ g/ml.

4.3 Nitric acid, $\varrho_{20} = 1,42$ g/ml.

4.4 Hydrochloric acid, $\varrho_{20} = 1,19$ g/ml.

4.5 Hydrochloric acid, approximately 0,3 mol/l solution.

Dilute 10 ml of the hydrochloric acid (4.4) to 1 litre with water.

4.6 Tin(II) chloride, solution containing 100 g of $SnCl_2.2H_2O$ per litre.

Prepare this solution on the day of use by one of the following two methods :

a) Dissolve 25 g of tin(II) chloride dihydrate in 50 ml of warm hydrochloric acid (4.4). If cloudy, filter and add a small granule of tin to the filtrate. Cool and transfer quantitatively to a 250 ml one mark volumetric flask. Dilute to the mark with water and mix.

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[1] If the reagents used lead to high results in blank tests, it is necessary to use products of better quality.

b) Dissolve, by heating in a boiling water bath, 13 g of tin in 50 ml of the hydrochloric acid (4.4). Cool, transfer quantitatively to a 250 ml one-mark volumetric flask, dilute to the mark with water and mix.

Eliminate any mercury which may be present in this solution by bubbling nitrogen through it (for example during 30 min).

4.7 Potassium dichromate, 4 g/l acidic solution.

Dissolve 4 g of potassium dichromate ($K_2Cr_2O_7$) in 500 ml of water and carefully add either 500 ml of the sulfuric acid (4.2) or 500 ml of the nitric acid (4.3).

4.8 Mercury, standard solution corresponding to 1 g of Hg per litre.

Weigh, to the nearest 0,001 g, 1,354 g of mercury(II) chloride ($HgCl_2$), transfer to a 1 000 ml one-mark volumetric flask and dissolve in about 25 ml of the hydrochloric acid (4.4). Dilute to the mark with water and mix. 1 ml of this standard solution contains 1 mg of Hg.

This solution can be stored in borosilicate glass bottles for about 1 month.

NOTE — This solution can be stabilized by adding 50 ml of the acidic potassium dichromate solution (4.7) before diluting to the mark.

4.9 Mercury, standard solution corresponding to 10 mg of Hg per litre.

Dilute 10,0 ml of the standard mercury solution (4.8) to 1 000 ml with the hydrochloric acid solution (4.5).

1 ml of this standard solution contains 10 µg of Hg.

Prepare this solution on the day of use.

4.10 Mercury, standard solution corresponding to 0,1 mg of Hg per litre.

Dilute 10,0 ml of the standard mercury solution (4.9) to 1 000 ml with the hydrochloric acid solution (4.5).

1 ml of this standard solution contains 0,1 µg of Hg.

Prepare this solution on the day of use.

5 Apparatus

Before use, all glassware shall be washed very carefully with the acidic potassium dichromate solution (4.7), and then rinsed several times with water (4.1).

Never dry the glassware between two operations.

5.1 Atomic absorption spectrometer, provided with a low pressure mercury lamp (or a hollow-cathode mercury lamp), or a **mercury vapour analyser.**

5.2 Recorder, with a maximum signal indicator or a peak area integrator (see note to 5.9).

5.3 Immersion-type ultraviolet lamp, medium or low pressure.[1]

NOTES

1 With the medium pressure lamps, sample cooling is essential either by means of an ice bath or using a water jacket through which chilled water is circulated around the irradiation vessel. In addition, some lamps require gas cooling as specified by the manufacturer. Some lamps will not relight for up to 20 min after being switched off and are best left switched on continuously during the tests.

2 Ultraviolet radiation is harmful to the skin and especially to the eyes. The lamps should be operated only when covered by an amber glass screen.

5.4 Irradiation vessels, of glass capable of containing at least 100 ml of sample and suitable for use with the UV lamp to be used. Suitable types of equipment are shown in figures 1, 2 and 3.

NOTE — The irradiation vessels should be designed so that the solution is exposed to the whole of the quartz window of the lamp. The efficiency of irradiation is closely dependent on effective mixing. A 250 ml measuring cylinder is the most suitable vessel for use with the Hanau lamps; its effectiveness is greatly increased by providing a loop between the bottom of the cylinder and the liquid surface which allows the magnetic stirrer to act as a circulation pump. The Hanovia lamps require special irradiation vessels, but the same principles apply.

It is essential that the combination of the UV lamp and the irradiation vessels be checked before use to ensure that complete destruction of organic mercury compounds occurs in an acceptably short time. As the lamp ages, repeat checks should be carried out to confirm that the time initially established is still valid (a method of control is described in annex B).

5.5 Aeration flasks.

The aeration may be carried out in the irradiation vessel if it has a suitable shape. If not, the irradiated solution should be transferred to a tall form aeration flask, of volume appropriate to the size of the test portion, compatible with the rest of the apparatus, bearing a calibration mark corresponding to the optimum filling level, the dead volume of which has been reduced to a minimum and through which the gas flows under the optimum conditions. For this, the aeration tube should be designed with a finely drawn out point, a sphere pierced with holes or a fritted end (pores of 100 to 250 µm). It is necessary to confirm that the different flasks used all lead to the same result.

After each use, treat the aeration flasks with the acidic potassium dichromate solution (4.7) to oxidize any traces of tin(II) that they may contain.

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1) Medium pressure lamps such as the Hanau TQ 150 and TQ 150/Z3, Hanovia PCR1L and the low pressure lamp Hanau TNN 15/32 are satisfactory.

5.6 Magnetic stirrers, with a large bar for the ice bath and with a small bar for the irradiation vessel.

5.7 Measuring cell, with windows of quartz or of other material transparent to the ultraviolet radiation (about 253,7 nm), the length of which is appropriate to the spectrometer being used.

5.8 Equipment to avoid, if necessary, any condensation of water vapour in the interior of the measuring cell. Any appropriate system may be used for this purpose (infra-red lamp, black electrical heating element, rod heater, desiccant trap, etc.).

5.9 Equipment for absorption of mercury vapour as it leaves the measuring cells, containing, for example, 2,5 g/l iodine solution in 30 g/l potassium iodide solution.

NOTE — It is possible to use a closed-circuit aeration system, in which the mercury vapour is recycled by means of a pump. In this case a recorder is no longer necessary and it is possible to use a direct reading instrument or a maximal signal indicator.

6 Samples

Immediately after collection treat each sample with 50 ml of acidic potassium dichromate solution (4.7), as preservative, for each litre of sample.

7 Procedure

7.1 Test portion

Take a test portion of 100 ml from the previously mixed sample (clause 6).

7.2 Calibration

Prepare, at the moment of use, using the standard mercury solutions (4.9 and 4.10), at least five calibration solutions covering the range of concentrations which can be measured with the apparatus to be used (depending on the circumstances, this range may cover a part or the whole of the range 0,1 to 10 µg of mercury per litre).

Treat each of these solutions immediately after their preparation in exactly the same way as the test portion on which the determination is to be carried out (see 7.3.1 and 7.3.2).

Also proceed in exactly the same way, replacing the test portion with the water (4.1) (zero term).

As appropriate, measure either the peak heights in centimetres or the peak areas in square centimetres and plot a calibration graph.

7.3 Determination

7.3.1 Mineralization by irradiation

Assemble the photochemical reactor and, where applicable, flush with nitrogen. Switch on the lamp (5.3) and allow it to warm up for several minutes before beginning irradiation.

Transfer the test portion (7.1) to an irradiation vessel (5.4) and insert the small bar of the magnetic stirrer (5.6).

Attach the vessel to the photochemical reactor and surround with an ice bath. Irradiate the test solution for 10 min, while stirring continuously.

7.3.2 Entrainment and determination

Remove the irradiation vessel from the photochemical reactor. If it is not of suitable shape, transfer the irradiated solution to an aeration flask (5.5). Adjust the temperature to 20 ± 0,5 °C [unless the spectrometer (5.1) is fitted with a drying tube], and add 2 ml of the tin(II) chloride solution (4.6). Immediately connect the aeration flask to the aeration apparatus, swirl to mix, and begin the aeration 30 s after the addition of the tin(II) chloride.

The entrainment of the mercury through the measuring cell (5.7) produces a peak on the recorder which rapidly attains a maximum.

If peak heights are being used as a measure of response, purge the gas circuit and replace the aeration flask with one containing water as soon as the absorbance begins to decrease. If peak areas are being used do not interrupt the recording until the signal has returned to its initial value.

NOTE — If the peak obtained during a determination does not have the same shape as that obtained from a standard solution, it is recommended that peak areas be measured and not peak heights. In all cases, the absence of interferences should be verified by means of the control test (7.5).

7.4 Blank test

Carry out a blank test, proceeding as specified in 7.3.1 and 7.3.2, but replacing the test portion by water (4.1), and using the same volumes of reagents as for the determination proper.

Make allowance for the volumes of reagent added during collection of the samples (see clause 6).

Determine the blank value for each batch of samples (see annex A).

7.5 Control test

In the case of drinking water and water used for food and drink processing, interferences are unlikely to occur. In cases of doubt, an indication of possible interferences can be obtained by repeating the operations specified in 7.3.1 and 7.3.2 using a new test portion taken from the sample (clause 6) or using an aliquot part of it to which a known quantity of standard mercury solution (4.10) has been added.

8 Expression of results

The total mercury content, expressed in micrograms per litre, is given by the formula

$$(m_1 - m_0) \times 10 \times 1,05$$

where

m_0 is the mass, in micrograms, of mercury found in the blank test (7.4);

m_1 is the mass, in micrograms of mercury found in the determination (7.3.2);

1,05 is a factor to take into account the dilution of the sample due to the addition of the preservative (4.7) (see clause 6).

9 Precision

A joint ISO and BITC (Bureau international technique du chlore) interlaboratory test was carried out, in November 1977,

on a first sample (A) containing 0,58 µg of mercury per litre, and on a second sample (B) containing 0,67 µg of mercury per litre and 1,5 mg of iodide ions per litre.

Statistical analysis of the results in accordance with ISO 5725 has given information shown below.

10 Test report

The test report shall include the following information :

a) all information necessary for complete identification of the sample;

b) the method used;

c) the results obtained;

d) the conditions of test;

e) details of any operations not included in this International Standard, or regarded as optional, together with any incidents likely to have had an influence upon the results.

| Sample | Number of participating laboratories | Number of eliminated laboratories | Mean µg/l | Standard deviation | | | |
| | | | | Repeatability | | Reproducibility | |
				Absolute	Relative	Absolute	Relative
A	25	0	0,568 7	0,033	5,8 %	0,170	29,9 %
B	25	2	0,643 9	0,040	6,3 %	0,208	32,2 %

Dimensions in millimetres

Gas purge inlet

Cooling water inlet
(optional)

Water exit

Hanovia medium pressure
UV lamp
PCR1L

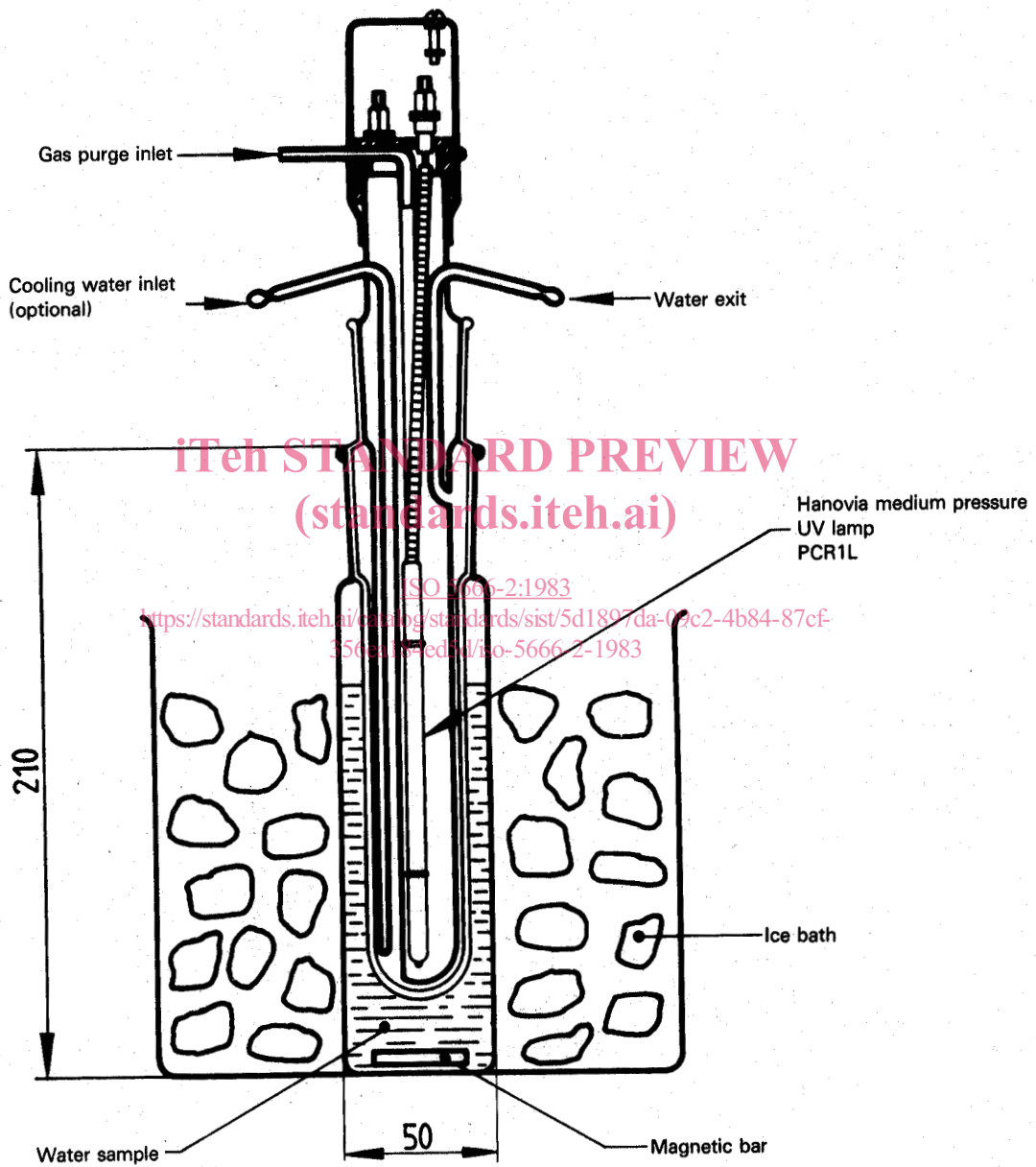Ice bath

Water sample

50

Magnetic bar

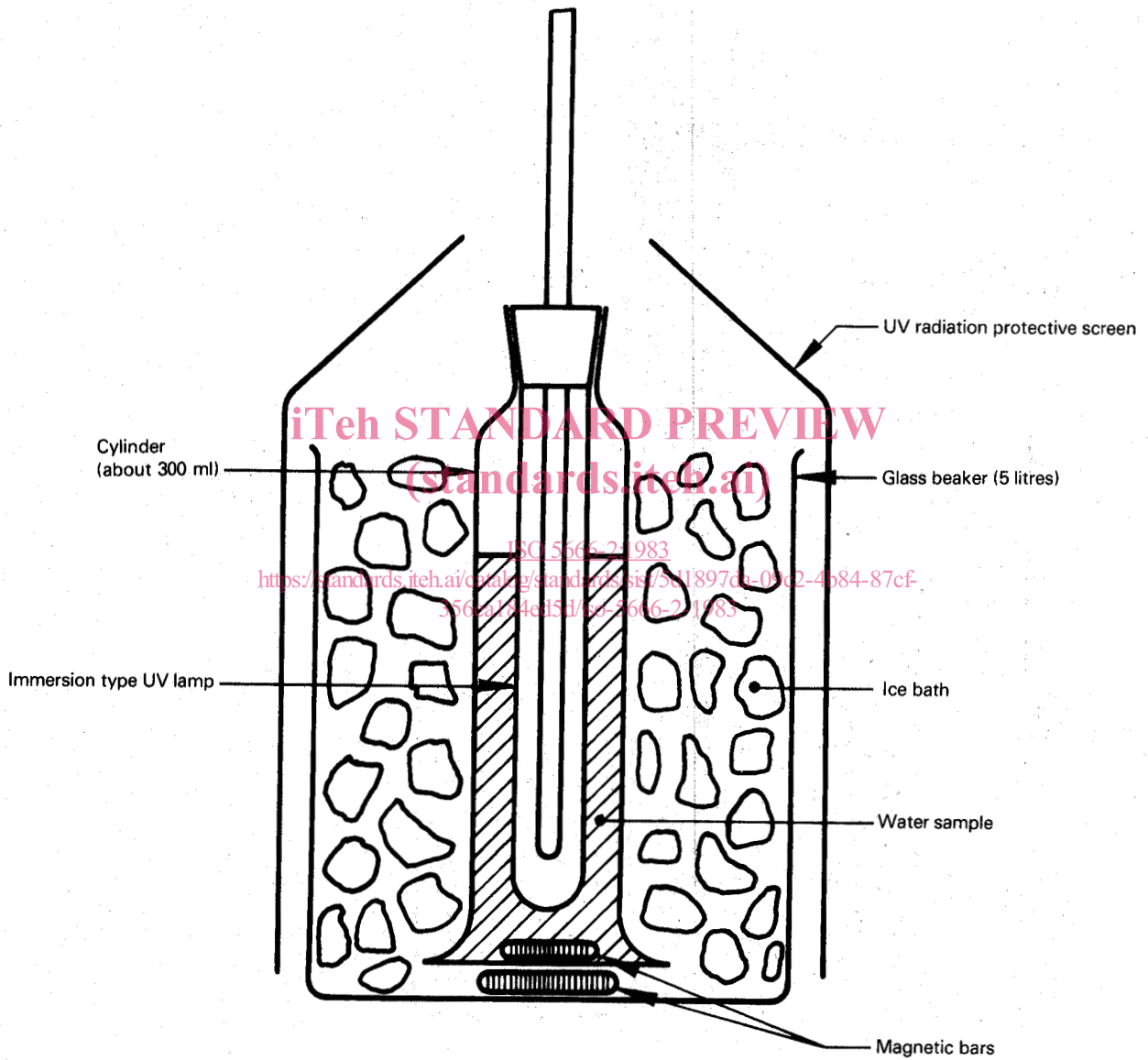Figure 1 — Apparatus for UV irradiation (capacity 100 ml)

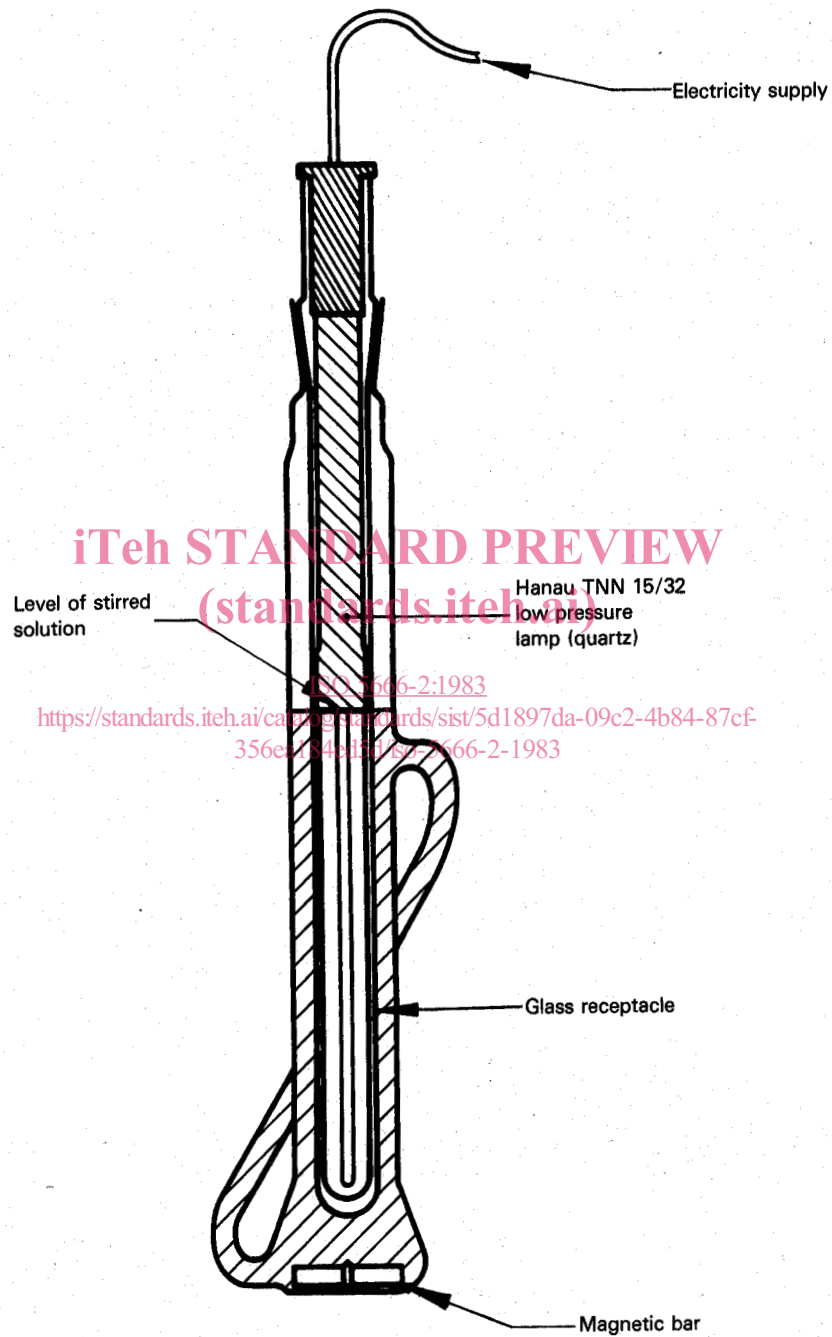**Figure 2 — Apparatus for UV irradiation** (capacity 100 ml, Winkler type)

Figure 3 — Apparatus for UV irradiation (capacity 170 ml)