

COUNCIL DIRECTIVE

of 15 July 1980

on air quality limit values and guide values for sulphur dioxide and suspended particulates

(80/779/EEC)

THE COUNCIL OF THE EUROPEAN COMMUNITIES,

Having regard to the Treaty establishing the European Economic Community, and in particular Articles 100 and 235 thereof,

Having regard to the proposal from the Commission,

Having regard to the opinion of the European Parliament ⁽¹⁾,

Having regard to the opinion of the Economic and Social Committee ⁽²⁾,

Whereas the European Communities' programmes of action on the environment of 1973 ⁽³⁾ and 1977 ⁽⁴⁾ provide that priority is to be given to measures against sulphur dioxide and suspended particulates because of their toxicity and the current state of knowledge of their effects on human health and the environment;

Whereas, since any discrepancy between the provisions already applicable or being prepared in the various Member States with regard to sulphur dioxide and suspended particulates could give rise to unequal conditions of competition and could consequently directly affect the functioning of the common market, the legislative provisions in this area should be harmonized as prescribed in Article 100 of the Treaty;

Whereas one of the basic tasks of the European Economic Community is to promote throughout the Community a harmonious development of economic activities and a continued and balanced expansion; whereas such an achievement is inconceivable without measures to combat pollution, improve the quality of life and protect the environment; whereas, since the Treaty has not provided the necessary powers in this field, Article 235 of the Treaty must be invoked;

Whereas, in order to protect human health in particular, it is necessary to set for these two pollutants limit values which must not be exceeded in the territory of the Member States during specified periods; whereas these values should be based on the findings reached in the framework of the WHO, particularly with regard to the dose/effect relationships established for sulphur dioxide and suspended particulates taken together;

Whereas, despite the measures taken, it may not be possible to comply with these limit values in certain zones; whereas the Member States must therefore be allowed temporary derogations on condition that they forward to the Commission plans for the progressive improvement of the quality of the air in those zones;

Whereas guide values should also be set to serve as long-term precautions for health and the environment and as reference points for the establishment of specific schemes within zones determined by the Member States;

Whereas the measures taken pursuant to this Directive must be economically feasible and compatible with balanced development;

Whereas it is necessary to establish suitable monitoring of air quality and particularly of observance of the limit values; whereas the Member States should therefore be obliged to establish measuring stations to supply the data necessary for the application of the Directive;

Whereas since different sampling and analysis methods are applied in the Member States, it is necessary to permit, under certain conditions, the use of sampling and measurement methods other than the reference methods laid down in the Directive;

Whereas, since some Member States use particular methods of sampling and analysis which cannot easily be correlated with the reference methods, it is necessary that the Directive specify different limit values which are to be respected where such methods are used; whereas the Member States concerned should also carry out parallel measurements at a series of representative

(1) OJ No C 83, 4. 4. 1977, p. 44.

(2) OJ No C 204, 30. 8. 1976, p. 34.

(3) OJ No C 112, 20. 12. 1973, p. 1.

(4) OJ No C 139, 13. 6. 1977, p. 1.

stations using the reference methods in addition to their own methods of measurement; whereas the Commission must make further proposals in the light of these parallel measurements and of the need to avoid discriminatory provisions;

Whereas the subsequent development of reference methods of sampling and analysis referred to in this Directive may be desirable in the light of technical and scientific progress in this area; whereas in order to facilitate implementation of the work necessary to this end, a procedure should be set up to establish close cooperation between the Member States and the Commission within a Committee on Adaptation to Scientific and Technical Progress,

HAS ADOPTED THIS DIRECTIVE:

Article 1

The purpose of this Directive is to fix limit values (Annex I) and guide values (Annex II) for sulphur dioxide and suspended particulates in the atmosphere and the conditions for their application in order to improve:

- the protection of human health,
- the protection of the environment.

Article 2

1. 'Limit values' means:

- the concentrations of sulphur dioxide and suspended particulates considered simultaneously in accordance with Table A in Annex I, and
- the concentrations of suspended particulates considered separately in accordance with Table B in Annex I,

which, in order to protect human health in particular, must not be exceeded throughout the territory of the Member States during specified periods and under the conditions laid down in the following Articles.

2. 'Guide values' means the concentrations of sulphur dioxide and suspended particulates over specified periods which are given in Annex II and are intended to serve as:

- long-term precautions for health and the environment,
- reference points for the establishment of specific schemes within zones determined by the Member States.

Article 3

1. Member States shall take appropriate measures to ensure that as from 1 April 1983 the concentrations of sulphur dioxide and suspended particulates in the atmosphere are not greater than the limit values given in Annex I, without prejudice to the following provisions.

2. Where a Member State considers that there is a likelihood that, despite the measures taken, the concentrations of sulphur dioxide and suspended particulates in the atmosphere might, after 1 April 1983, exceed in certain zones the limit values given in Annex I, it shall inform the Commission thereof before 1 October 1982.

It shall at the same time forward to the Commission plans for the progressive improvement of the quality of the air in those zones. These plans, drawn up on the basis of relevant information on the nature, origin and evolution of the pollution, shall describe in particular the measures taken or to be taken and the procedures implemented or to be implemented by the Member State concerned. These measures and procedures must bring the concentrations of sulphur dioxide and suspended particulates in the atmosphere within these zones to values below or equal to the limit values given in Annex I as soon as possible and by 1 April 1993 at the latest.

Article 4

1. In the zones in which the Member State concerned considers it necessary to limit or prevent a foreseeable increase in pollution by sulphur dioxide and suspended particulates in the wake of development, in particular urban or industrial development, the Member State shall, taking the guide values in Annex II as a reference point, fix values which must be lower than the limit values in Annex I.

2. In zones on its territory which the Member State concerned considers should be afforded special environmental protection, the Member State shall fix values which are generally lower than the guide values in Annex II.

3. Member States shall inform the Commission of the values, deadlines and timetables they have laid down for the zones referred to in paragraphs 1 and 2, and of any appropriate measures they have taken.

Article 5

In addition to the provisions referred to in Article 3 (1) and Article 4 (1), Member States shall, with the object of taking further precautions for the protection of health and the environment, endeavour to move towards the guide values in Annex II wherever the measured concentrations are higher than these values.

Article 6

Member States shall establish measuring stations designed to supply the data necessary for the application of this Directive, in particular in zones where the limit values referred to in Article 3 (1) are likely to be approached or exceeded and in the zones referred to in Article 3 (2); the stations must be located at sites where pollution is thought to be greatest and where the measured concentrations are representative of local conditions.

Article 7

1. Following the entry into force of this Directive, Member States shall inform the Commission, not later than six months after the end (31 March) of the annual reference period, of instances in which the limit values laid down in Annex I have been exceeded and of the concentrations recorded.

2. They shall also notify the Commission, not later than one year after the end of the annual reference period, of the reasons for such instances and of the measures they have taken to avoid their recurrence.

3. In addition, Member States shall forward information to the Commission, at its request, on the concentrations of sulphur dioxide and suspended particulates in any zones they have designated pursuant to Article 4 (1) and (2).

Article 8

The Commission shall each year publish a summary report on the application of this Directive.

Article 9

Application of the measures taken pursuant to this Directive must not bring about a significant deterioration in the quality of the air where the level of pollution by sulphur dioxide and suspended particulates at the time of implementation of this Directive is low in relation to the limit values set out in Annex I.

Article 10

1. For the purposes of applying this Directive, the Member States shall use either the reference methods of sampling and analysis referred to in Annex III or any other method of sampling and analysis in respect of which they demonstrate to the Commission at regular intervals:

— either that it ensures satisfactory correlation of results with those obtained using the reference method;

— or that measurements taken in parallel with the reference method at a series of representative stations chosen in accordance with the requirements laid down in Article 6 show that there is a reasonably stable relationship between the results obtained using that method and those obtained using the reference method.

2. Without prejudice to the provisions of this Directive, a Member State may also use, pending the decision of the Council on the proposals from the Commission referred to in paragraph 4, the sampling and analysis methods laid down in Annex IV and the values associated with these methods also laid down in Annex IV in substitution for the limit values set out in Annex I.

3. A Member State which decides to avail itself of the provisions of paragraph 2 must however take measurements in parallel at a series of representative measuring stations, chosen in accordance with the requirements of Article 6, in order to verify the corresponding stringency of the limit values set out in Annex IV and Annex I. The results of these parallel measurements, including in particular instances in which the limit values laid down in Annex I have been exceeded and the concentrations recorded, shall be forwarded to the Commission at regular intervals, and at least twice a year, for incorporation in the annual report provided for in Article 8.

4. The Commission shall, after five years, but within six years of the expiry of the limit of 24 months specified in Article 15 (1), submit a report to the Council on the results of the parallel measurements carried out under paragraph 3 and shall, having regard in particular to these results and to the need to avoid discriminatory provisions, make proposals relating to paragraph 2 and Annex IV. In the report provided for in Article 8 the Commission will indicate whether it has noted instances in which the limit values fixed in Annex I have been exceeded to a significant extent on repeated occasions.

5. The Commission shall, in selected locations in the Member States and in cooperation with the latter, carry out studies on the sampling and analysis of sulphur dioxide, and of black smoke and suspended particulates. These studies shall be designed in particular to promote the harmonization of methods of sampling and analysis of these pollutants.

Article 11

1. Where Member States fix in border regions values for concentrations of sulphur dioxide and suspended particulates in the atmosphere in accordance with Article 4 (1) and (2), they shall hold prior consultations. The Commission may attend such consultations.

2. Where the limit values given in Annex I or the values referred to in Article 4 (1) and (2), inasmuch as

the latter values have been the subject of consultations in accordance with paragraph 1, are or might be exceeded following significant pollution which originates or may have originated in another Member State, the Member States concerned shall hold consultations with a view to remedying the situation. The Commission may attend such consultations.

Article 12

The procedure laid down in Articles 13 and 14 for the adaptation on this Directive to technical progress shall cover the subsequent development of the reference methods of sampling and analysis referred to in Annex III. This adaptation must not result in any direct or indirect modification of effective concentration values given in Annexes I and II.

Article 13

1. For the purpose of Article 12 a Committee on the adaptation of this Directive to scientific and technical progress, hereinafter called 'the Committee', shall be set up; it shall consist of representatives of the Member States, with a Commission representative as chairman.
2. The Committee shall adopt its own rules of procedure.

Article 14

1. Where the procedure laid down in this Article is invoked, the Committee shall be convened by the chairman, either on his own initiative or at the request of the representative of a Member State.
2. The Commission representative shall submit a draft of the measures to be taken to the Committee. The Committee shall give its opinion on the draft within a time limit set by the chairman having regard to the urgency of the matter. Decisions shall be taken by a majority of 41 votes, the votes of the Member States

being weighted as provided in Article 148 (2) of the Treaty. The chairman shall not vote.

3. The Commission shall adopt the proposed measures if they are consistent with the opinion of the Committee.

Where the proposed measures are not consistent with the opinion of the Committee, or if no opinion is delivered, the Commission shall without delay submit to the Council a proposal on the measures to be taken. The Council shall decide by a qualified majority.

If within three months of the proposal being submitted to it the Council has not acted, the proposed measures shall be adopted by the Commission.

Article 15

1. Member States shall bring into force the laws, regulations and administrative provisions necessary to comply with this Directive within 24 months of its notification and shall forthwith inform the Commission thereof.
2. Member States shall communicate to the Commission the texts of the provisions of national law which they adopt in the field covered by this Directive.

Article 16

This Directive is addressed to the Member States.

Done at Brussels, 15 July 1980.

For the Council

The President

J. SANTER

ANNEX I

LIMIT VALUES FOR SULPHUR DIOXIDE AND SUSPENDED PARTICULATES

(As measured by the black-smoke method)

TABLE A

Limit values for sulphur dioxide expressed in $\mu\text{g}/\text{m}^3$ with the associated values for suspended particulates (as measured by the black-smoke method ⁽¹⁾) expressed in $\mu\text{g}/\text{m}^3$

Reference period	Limit value for sulphur dioxide	Associated value for suspended particulates
Year	80 (median of daily mean values taken throughout the year)	> 40 (median of daily mean values taken throughout the year)
	120 (median of daily mean values taken throughout the year)	\leq 40 (median of daily mean values taken throughout the year)
Winter (1 October to 31 March)	130 (median of daily mean values taken throughout the winter)	> 60 (median of daily mean values taken throughout the winter)
	180 (median of daily mean values taken throughout the winter)	\leq 60 (median of daily mean values taken throughout the winter)
Year (made up of units of measuring periods of 24 hours)	250 ⁽²⁾ (98 percentile of all daily mean values taken throughout the year)	> 150 (98 percentile of all daily mean values taken throughout the year)
	350 ⁽²⁾ (98 percentile of all daily mean values taken throughout the year)	\leq 150 (98 percentile of all daily mean values taken throughout the year)

⁽¹⁾ The results of the measurements of black smoke taken by the OECD method have been converted into gravimetric units as described by the OECD (see Annex III).

⁽²⁾ Member States must take all appropriate steps to ensure that this value is not exceeded for more than three consecutive days. Moreover, Member States must endeavour to prevent and to reduce any such instances in which this value has been exceeded.

TABLE B

Limit values for suspended particulates (as measured by the black-smoke method ⁽¹⁾)
expressed in $\mu\text{g}/\text{m}^3$

Reference period	Limit value for suspended particulates
Year	80 (median of daily mean values taken throughout the year)
Winter (1 October to 31 March)	130 (median of daily mean values taken throughout the winter)
Year (made up of units of measuring periods of 24 hours)	250 ⁽²⁾ (98 percentile of all daily mean values taken throughout the year)

⁽¹⁾ The results of the measurements of black smoke taken by the OECD method have been converted into gravimetric units as described by the OECD (see Annex III).

⁽²⁾ Member States must take all appropriate steps to ensure that this value is not exceeded for more than three consecutive days. Moreover, Member States must endeavour to prevent and to reduce any such instances in which this value has been exceeded.

ANNEX II

GUIDE VALUES FOR SULPHUR DIOXIDE AND SUSPENDED PARTICULATES

(as measured by the black-smoke method)

TABLE A

(Guide values for sulphur dioxide expressed in $\mu\text{g}/\text{m}^3$)

Reference period	Guide value for sulphur dioxide
Year	40 to 60 (arithmetic mean of daily mean values taken throughout the year)
24 hours	100 to 150 (daily mean value)

TABLE B

Guide values for suspended particulates (as measured by the black-smoke method ⁽¹⁾)
expressed in $\mu\text{g}/\text{m}^3$

Reference period	Guide value for suspended particulates
Year	40 to 60 (arithmetic mean of daily mean values taken throughout the year)
24 hours	100 to 150 (daily mean value)

⁽¹⁾ The results of the measurements of black smoke taken by the OECD method have been converted into gravimetric units as described by the OECD (see Annex III).

ANNEX III**REFERENCE METHODS OF SAMPLING AND ANALYSIS TO BE EMPLOYED WITHIN THE
CONTEXT OF THIS DIRECTIVE****A. SULPHUR DIOXIDE**

The reference method of sampling for the determination of sulphur dioxide uses the equipment described in International Standard ISO-4219, first edition 1979/09/15. The sampling period is normally 24 hours.

The reference method of analysis is that described in detail in Annex V; it is based on Draft International Standard ISO DP-6767, revised February 1979 : 'Air quality — determination of the mass concentration of sulphur dioxide in ambient air — tetrachloromercurate (TCM)/pararosaniline'. This method of analysis is based on the principle of the colorimetric reaction with pararosaniline.

B. SUSPENDED PARTICULATES

For the determination of black smoke and its conversion into gravimetric units, the method standardized by the OECD working party on methods of measuring air pollution and survey techniques (1964) is considered to be the reference method.

For the above-noted methods, standardized respectively by ISO and OECD, the linguistic versions published by these organizations will be regarded as authentic together with the other versions which the Commission will certify as being in conformity therewith.

ANNEX IV

LIMIT VALUES FOR SULPHUR DIOXIDE AND SUSPENDED PARTICULATES (AS MEASURED BY A GRAVIMETRIC METHOD) APPLICABLE WITHIN THE CONTEXT OF ARTICLE 10 (2)

TABLE A
Limit values for sulphur dioxide expressed in $\mu\text{g}/\text{m}^3$

Reference period	Limit value for sulphur dioxide
Year	140 (arithmetic mean of 30 minute values taken throughout the year)
Year (made up of units of measuring periods of 30 minutes)	400 (95 percentile of all 30 minute values taken throughout the year)

TABLE B
Limit values for suspended particulates (as measured by the gravimetric method described in (ii) below) expressed in $\mu\text{g}/\text{m}^3$

Reference period	Limit value for suspended particulates
Year	150 (arithmetic mean of daily mean values taken throughout the year)
Year (made up of units of measuring periods of 24 hours)	300 (95 percentile of all daily mean values taken throughout the year)

The methods of sampling and analysis applicable within the context of Article 10 (2) are with respect to:

(i) Sulphur dioxide

— *Method of sampling:* measuring stations permitting 'random' sampling are used with a grid network of the type represented by Figure 1. At each point of the network at least 13 samples per year are taken between 8 a.m. and 4 p.m. on working days. The different samples are collected for 30 minutes continuous duration at regular intervals throughout the year, for example as follows:

On the first day, samples are taken at the points marked 'a' in Figure 1, on the second day on the points marked 'b', on the third day at the points marked 'c' and on the fourth day at the points marked 'd'. These samplings are repeated for each point at intervals of four weeks for different periods of 30 minutes chosen 'at random'.

- Evaluation period: one year,
- number of points: 16 in a grid network,
- sampling duration: 30 minutes continuous between 8 a.m. and 4 p.m. on working days,
- number of samples per point: at least 13,
- total number of samples: at least 208.

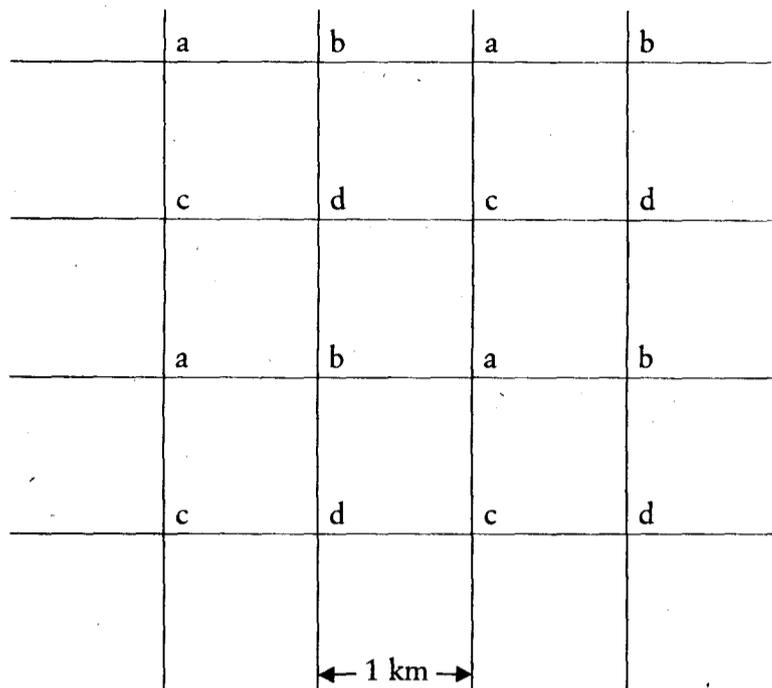


Figure 1

Sampling scheme

— *Method of analysis:* the reference method of Annex III. The procedure set out in Article 10 (1) applies.

(ii) Suspended particulates

— *Method of sampling:*

1. The suspended particulates are collected on a filter composed of either membrane or glass-fibre.
2. The sampling system consists of:
 - a filter,
 - a filter support,
 - a pump,
 - a volumetric gasmeter.
3. The sampling system does not include a fractionating device.
4. The sampling duration is 24 hours.
5. The filter is protected against direct deposition of particles by sedimentation and against the direct influence of atmospheric conditions.
6. The filters used should have an efficiency of more than 99 % for particles having an aerodynamic diameter of 0.3 μm .
7. The air velocity at the surface of the filter is between 33 and 55 cm/sec inclusive. The reduction in the speed throughout the sampling duration must not exceed 5 % if glass-fibre filters are used or 25 % if membrane filters are used.
8. The number of samplings made throughout the year must be at least 100, uniformly spread throughout this period.

— *Method of analysis:*

- (a) Analysis is by weighing.
 - (b) 1. Membrane filters are to be conditioned, before and after sampling, by holding them at a constant temperature between 90 and 100 °C for two hours and subsequently storing them in a dessicator for two hours before weighing.
 - (b) 2. Glass-fibre filters are to be conditioned, before and after sampling, by holding them for a period of 24 hours in an atmosphere at 20 °C and 50 % relative humidity before weighing.

ANNEX V

REFERENCE METHOD OF ANALYSIS FOR SULPHUR DIOXIDE

Air quality — Determination of the mass concentration of sulphur dioxide in ambient air —
Tetrachloromercurate (TCM)/pararosaniline method

1. SCOPE

This draft international standard specifies a spectrophotometric method for the determination of the mass concentration of sulphur dioxide in ambient air. The standard comprises methods for both sampling and analysis.

2. FIELD OF APPLICATION

With the procedure described in this standard, atmospheric sulphur dioxide concentrations between 7 and 1 150 $\mu\text{g}/\text{m}^3$ can be determined.

Note

If higher concentrations have to be determined aliquots of the sample solution or smaller air samples than specified in this standard can be taken. In this case the absorption efficiency of the concentrations under study.

Interferences from heavy metals, oxides of nitrogen, ozone and reduced sulphur compounds (e.g. hydrogen sulphide and mercaptanes) are eliminated or minimized. Sulphuric acid and sulphates do not interfere. No interference of sulphur trioxide has been experimentally ascertained, since this presumably becomes hydrated to sulphuric acid in the absorbing solution.

3. PRINCIPLE

A measured air sample is drawn through a solution of sodium tetrachloromercurate (TCM) and the sulphur dioxide present in the air is absorbed by formation of a dichlorosulphitomercurate complex.

The sample solution is treated with a solution of sulphamic acid to destroy the nitrite anion formed by the oxides of nitrogen present in the air. It is then treated with solutions of formaldehyde and acid-bleached pararosaniline containing phosphoric acid to obtain a pH of 1.6 ± 0.1 .

Pararosaniline, formaldehyde and the bisulphite anion react to form the intensely coloured pararosaniline methyl sulphonic acid, which behaves as a two-colour indicator ($\lambda_{\text{max}} = 548 \text{ nm}$ at pH 1.6 ± 0.1).

The concentration of sulphur dioxide is taken from a calibration graph prepared on the basis of calibration gas mixtures (6.3.1). According to the equipment available in the laboratory it may be convenient in certain cases, for routine checks to replace the calibration gas mixtures by sodium bisulphite solutions of known concentration. However, this procedure should only be used after a proper calibration with a permeation device.

4. REAGENTS

4.1. All reagents shall be of analytical quality (pro analysi).

Unless otherwise indicated, references to water shall mean distilled water. The water must be free from oxidants and should preferably be double-distilled from an all-glass apparatus.

4.2. Absorbing solution: 0.04 moles/l sodium tetrachloromercurate (TCM).

Dissolve 10.9 g of mercury (II) chloride, 4.7 g of sodium chloride and 0.07 g of ethylenediamine tetracetic acid disodium salt (EDTA) in water and dilute to 1 litre.

The solution is stable for several months and should be discarded if a precipitate is formed.

Notes

1. The amount of EDTA added eliminates possible interferences from heavy metals up to 60 µg of iron (III), 10 µg of manganese (II), 10 µg of chromium (III), 10 µg of copper (II) and 22 µg of vanadium (V) in 10 ml of absorbing solution.
2. The solution is highly poisonous and should be handled as such. A method for recovering the mercury after the analysis is given in Annex C. If any absorbing solution is spilt on the skin, it must be flushed off with water immediately.

4.3. Hydrochloric acid, 1 mole/l

Dilute 86 ml of concentrated hydrochloric acid, HCl ($\rho = 1.19$ g/ml, to 1 litre.

4.4. Pararosaniline hydrochloride, 0.2 % stock solution

Dissolve 0.2 g of pararosaniline hydrochloride, $C_{19}H_{17}N_3 \cdot HCl$ in 100 ml of hydrochloric acid (4.3).

Note

Pararosaniline hydrochloride used in the preparation of the stock solution must have a purity higher than 95 % (see Annex D) and exhibit a maximum absorption at 540 nm in acetic acid — sodium acetate buffer (0.1 moles/l). Furthermore, the absorbance of the reagent blank should not exceed 0.10 when the blank is prepared according to the procedure described in section 6.2.

Reagents that do not meet these requirements must be rejected or purified. The purification can be achieved by crystallization or extraction (see Annex D).

4.5. Phosphoric acid, 3 moles/l

Dilute 205 ml of concentrated phosphoric acid, H_3PO_4 , ($\rho = 1.69$ g/ml) with water to 1 litre.

4.6. Pararosaniline reagent solution

Pipet 20 ml of the pararosaniline hydrochloride stock solution (4.4) and 25 ml of phosphoric acid (4.5) into a 250 ml volumetric flask and make up to the mark with water.

This reagent is stable for several months if stored in the dark.

4.7. Formaldehyde, working solution

Pipet 5 ml of a 40 % formaldehyde solution, HCHO, into a 1 litre volumetric flask and make up to the mark with water. Prepare daily.

4.8. Sulphamic acid, 0.6 % working solution

Dissolve 0.6 g of sulphamic acid, NH_2SO_3H , in 100 ml water. This solution is stable for a few days if protected from air.

4.9. Sodium bisulphite solution. Stock solution

Dissolve 0.3 g of sodium metabisulphite, $Na_2S_2O_5$, in 500 ml of freshly boiled and cooled distilled water (double-distilled water that has been deaerated is preferred). The solution contains from 320 to 400 µg of sulphur dioxide equivalents per millilitre. The actual concentration is determined by adding an excess of iodine to an aliquot of the solution and back titrating with standardized sodium thiosulphate solution (see Annex B).

The solution is unstable.

4.10. Sodium bisulphite standard solution

Immediately after the standardization of the sodium bisulphite stock solution (4.9), pipet 2.0 ml of the solution into a 100 ml volumetric flask and make up to the mark with the sodium tetrachloromercurate solution (4.2).

This solution is stable for 30 days if stored at 5 °C. Stored at room temperature, it will be stable for one day only.

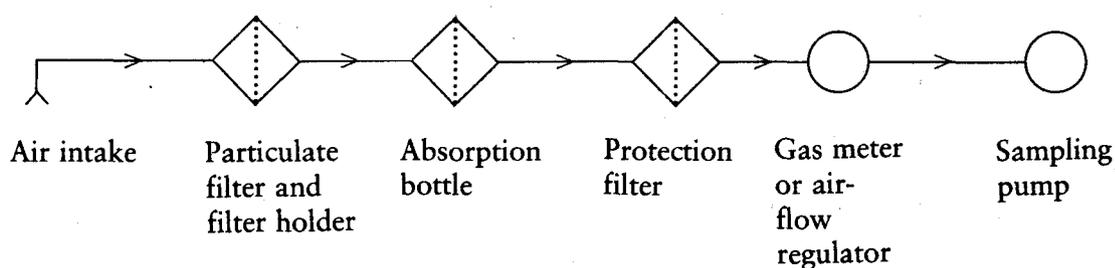
5. APPARATUS

5.1. Sampling equipment

The equipment to be used for sampling is specified in ISO/DIS 4219, Air Quality — Determination of gaseous compounds in ambient air — Sampling equipment as shown in Figure 1.

Figure 1

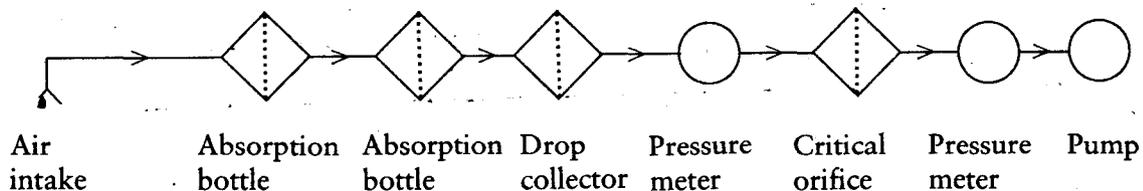
Block diagram of sampling equipment



Alternatively to the gas meter a hypodermic needle can be used as a critical orifice in a thermostated box. In this case, the pump must be able to reach $p_d/p_u \leq 0.5$, p_d and p_u being the pressures downstream and upstream the needle respectively (see 5.5).

Figure 2

The equipment is shown in Figure 2.



5.2. Absorption bottles

Satisfactory absorption bottles should have an absorption efficiency for sulphur dioxide of at least 95 %. Examples of suitable absorption bottles are given in Annex A.

The absorption efficiency varies with the geometry of the bottle, the size of the gas bubbles and their contact time with the solution. It can be determined by inserting a second absorption bottle in series to the first one into the sampling system and relating the amount of sulphur dioxide found in the first bottle to the sum of the sulphur dioxide amount in the two bottles. When working with midjet impingers under the conditions described in section 6.1, the absorption efficiency has been found to be better than 98 %.

The use of mixtures of sulphur dioxide and air for calibration, as described in clause 6.3.1, automatically gives the absorption efficiency of the system.

5.3. Hydrogen sulphide absorber

A glass tube filled with quartz wool impregnated with a solution containing 0.5 % of silver sulphate, Ag_2SO_4 , and 2.5 % of potassium hydrogen sulphate, $KHSO_4$. The impregnation is made by passing the solution twice through the tube and then drying the quartz wool by heating in a nitrogen stream.

5.4. Sample bottles

Polyethylene bottles, 100 ml, for transferring the exposed absorption solutions to the laboratory.

5.5. Manometer

Two manometers accurate to 1 000 Pa, for measurement of pressures when using a critical orifice instead of a gas meter.

5.6. Spectrophotometer or colorimeter

A spectrophotometer or colorimeter suitable for measuring the absorbance at about 550 nm. With a spectrophotometer, a wavelength of 548 nm should be used. If a colorimeter is used, the filter should have its transmittance maximum at about 550 nm. Reagent blank problems may occur with apparatus having a greater spectral band width than 20 nm.

When measuring the absorbance use the same cell for samples and standard solutions. If more than one cell is used, the cells must be spectrophotometrically matched.

6. PROCEDURE**6.1. Sampling**

Transfer 10 ml of the TCM solution (4.2) to an absorption bottle and insert it into the sampling system (Figure 1). Shield the absorbing solution from direct sunlight during the sampling by covering the absorption bottle with a suitable wrapping, such as aluminium foil, to prevent decomposition. The duration and flow rate of the aspiration depend on the concentration of sulphur dioxide in the air.

With midjet impingers, the volume flow rate should be between 0.5 l/min and 1 l/min. The minimum quantity of air aspirated should be 25 litres.

To obtain the best results, flow rate and sampling time should be chosen to achieve an absorption of 0.5 to 3.0 µg (0.2 to 1.2 µl at 25 °C and 101.325 kPa) of sulphur dioxide per ml of absorbing solution.

If the air is believed to contain hydrogen sulphide this must be removed by a hydrogen sulphide absorber (5.3). Place the absorber between the particulate filter and the absorption bottle.

After sampling, determine the volume of air sampled, and note the atmospheric temperature and pressure (7.1, Note). If the sample must be stored for more than 24 hours before analysis, keep it at 5 °C.

Note

If the sample solution shows a precipitate, it is probably due to the reaction of Hg II with a reduced sulphur compound. Remove the precipitate by filtration or centrifugation before the analysis.

6.2. Analysis

Samples must be left for at least 20 minutes after sampling to allow trapped ozone to decompose. Then transfer the sample solution quantitatively to a 25 ml volumetric flask, using about 5 ml of water for rinsing.

Prepare a blank by adding 10 ml of unexposed absorbing solution (4.2) to a 25 ml volumetric flask, add the reagents as described below and read the absorbance against distilled water using 10 mm cells. Compare this value with the one recorded for the blank obtained when preparing the calibration curve. Differences of more than 10 % between the two values indicate contamination of the distilled water or the reagents or decomposition of the latter, in which case fresh reagents must be prepared.

Add 1 ml of the sulphamic acid solution (4.8) to each flask and allow to react for 10 minutes to destroy the nitrate from oxides of nitrogen. Then accurately pipet 2 ml of the formaldehyde solution (4.7) and 5 ml of the pararosaniline reagent (4.6) into the flasks. Make up to the mark with freshly boiled and cooled distilled water and store in a thermostat at 20 °C. After 30 to 60 minutes measure the absorbance of the sample and the blank with distilled water in the reference cell.

Do not let the coloured solution remain in the cell as a film of dye will then be deposited on the walls.

Note

Fixed time intervals between the addition of each reagent e.g. one minute ensure a better reproducibility of the colour development.

Solutions with absorbances exceeding that of the highest concentration used for calibration can be diluted up to sixfold with the reagent blank in order to obtain an on-scale reading. This reading, however, is only an indicative within $\pm 10\%$ of the true absorbance value.

6.3. Calibration

6.3.1. Calibration with a mixture of sulphur dioxide and air

Mixtures of sulphur dioxide and air are prepared according to ISO/DIS 6349.

In order to prepare the calibration graph, which is a plot of absorbance versus sulphur dioxide concentration, at least four different concentration levels of sulphur dioxide within the range prescribed in section 2 are needed.

The sampling procedure and the analytical procedure as described under 6.1 and 6.2, respectively, are applied to each of the calibration gas mixtures. The absorbance values are plotted against the given sulphur dioxide concentrations, and a calibration graph is prepared.

6.3.2. Calibration with sodium bisulphite solution

Pipet graduated amounts of the sodium bisulphite standard solution (4.10), 0, 1.0, 2.0, 3.0, 4.0 and 5.0 ml, into a series of 25 ml volumetric flasks. Add sufficient sodium tetrachloromercurate solution (4.2) to each flask to bring the volume to approximately 10 ml. Then add the reagents as described in 6.2. Measure the absorbances with distilled water in the reference cell. For higher precision it is necessary to use a constant-temperature bath. The temperature at the calibration should not differ from the temperature at the analysis by more than ± 1 °C.

Plot the absorbances of the solutions (as ordinates) against the microgrammes of sulphur dioxide calculated according to Annex B. A linear relationship is obtained. The intercept with the vertical axis of the line best fitting the points is usually within 0.02 absorbance units of the blank (zero standard) reading if 10 mm cells are used. Evaluate the calibration factor (reciprocal of the slope of the line). This calibration factor can be used for calculating the results, provided there are no radical changes in temperature or pH. At least one control sample is recommended per series of determinations to ensure the reliability of this factor.

7. EXPRESSION OF RESULTS

7.1. Calculation

Calculate the mass concentration of sulphur dioxide as follows:

$$SO_2 = \frac{f(a_s - a_b)}{V}$$

where

SO_2 = mass concentration of sulphur dioxide in micrograms per cubic metre

f = calibration factor (see 6.3.2)

a_s = Absorbance of the sample solution

a_b = absorbance of the blank

V = volume of air sampled, in cubic metres

Note

If the mass sulphur dioxide concentration at reference conditions (25 °C, 1 bar) is needed, the volume of air sampled, V , must be replaced by the corresponding value of volume under reference conditions, V_R :

$$V_R = \frac{298 V p}{273 + T}$$

where

p = barometric pressure, in bar

T = Temperature of air sample, in °C.

7.2. **Detection limit**

The detection limit of sulphur dioxide in 10 ml of TCM sampling solution is between 0.2 and 1.0 μg (based on twice the standard deviation). This corresponds to mass concentrations of sulphur dioxide of between 7 and 33 $\mu\text{g}/\text{m}^3$ (0.02 — 0.011 ppm) in air sample of 30 litres (e.g. one hour sampling at 0.5 l/min).

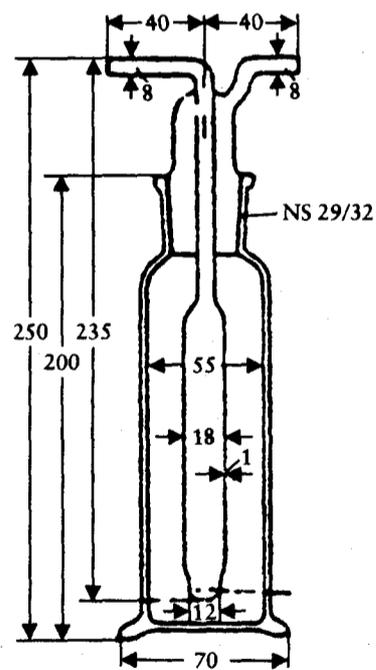
7.3. **Precision and accuracy**

The precision and accuracy of the method has not yet been determined to any degree of certainty over a variety of concentrations of sulphur dioxide, nor is the absolute collection efficiency known for the wide variety of possible systems of sampling and testing.

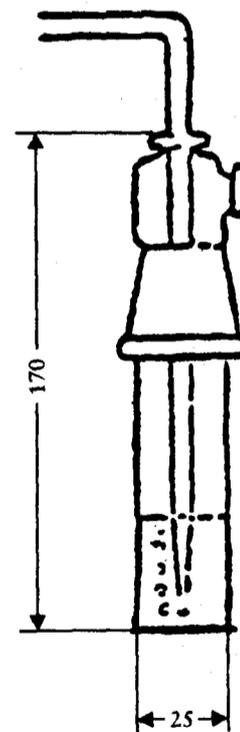
The relative standard deviation of a comparable TCM-method for replication has been found to be 17 $\mu\text{g}/\text{m}^3$ at a concentration of 1 000 $\mu\text{g}/\text{m}^3$ ⁽¹⁾.

8. **LITERATURE**

- ⁽¹⁾ H. C. McKee, R. E. Childers, O. Saenz: Collaborative Study of Reference Method for Determination of Sulphur Dioxide in the Atmosphere (Pararosaniline Method). Contract CPA 70—40, SwRI Project 21—2811. Environmental Protection Agency, Research Triangle Park, N. C., September 1971.

ANNEX A**ABSORBER MODELS****Muenke-flask**

75 ml four holes, one in bottom,
each 1.5 \varnothing

**Midget impinger**

ANNEX B

STANDARDIZATION OF THE SODIUM BISULPHITE STOCK SOLUTION (4.9)

B.1. Reagents

B.1.1. Iodine solution, 0.05 moles/l

Stock solution

Weigh 12.7 g of iodine, I₂, into a 250 ml beaker, add 40 g of potassium iodide, KI, and 25 ml of water. Stir until all is dissolved and transfer the solution quantitatively to a 1 litre volumetric flask. Dilute to the mark with water.

B.1.2. Iodine working solution, approximately 0.005 moles/l

Dilute 50 ml of the iodine stock solution (B. 1.1) to 500 ml with water.

B.1.3. Starch indicator solution, 0.2 %

Triturate 0.4 g of soluble starch and 0.002 g of mercury (II) iodide, HgI₂ (preservative), with a little water, and add the paste slowly to 200 ml of boiling water. Continue the boiling until the solution is clear, cool and transfer to a glass stoppered bottle.

B.1.4. Sodium thiosulphate solution, approximately 0.1 moles/l

Dissolve 25 g of sodium thiosulphate, Na₂S₂O₃·5 H₂O, in 1 litre of freshly boiled and distilled water and add 0.1 g of sodium carbonate to the solution. Allow the solution to stand for one day before standardizing.

To standardize, weigh 1.5 g of potassium iodate, KIO₃, primary standard grade, dried at 180 °C into a 500 ml volumetric flask and dilute to the mark with water. To a 500 ml iodine flask, pipet 50 ml of the iodate solution. Add 2 g of potassium iodide and 10 ml of a 1 : 10 dilution of concentrated hydrochloric acid. Stopper the flask. After five minutes titrate with sodium thiosulphate solution to a pale yellow colour. Add 5 ml of the starch indicator and complete the titration. Calculate the molarity of the sodium thiosulphate solution, M, as follows

$$M = \frac{\text{g KIO}_3 \times 10^3 \times 0.1}{\text{ml sodium thiosulphate solution} \times 35.67}$$

B.1.5. Sodium thiosulphate solution, approximately 0.01 moles/l

Dilute 50.0 ml of the sodium thiosulphate solution (B.1.4) to 500 ml with water and mix. The solution is not stable and must be prepared fresh on the day it is to be used by diluting the standardized sodium thiosulphate solution (B.1.4).

B.2. Procedure

Add 25 ml of water to a 500 ml flask and pipet 50 ml of the iodine solution (B 1.2) into the flask (here designated flask A/blank). Pipet 25 ml of the sodium bisulphite stock solution (4.9) to a second 500 ml flask and pipet 50 ml of iodine solution (B.1.2) into this flask (here designated B/sample). Stopper the flasks and allow to react for five minutes. By means of a burette containing sodium thiosulphate solution (B.1.5), titrate each flask in turn to a pale yellow colour. Then add 5 ml of starch solution (B.1.3) and continue the titration until the blue colour disappears. Calculate the concentration of sulphur dioxide in the sodium bisulphite stock solution (4.9):

$$\text{SO}_2 (\mu\text{g/ml}) = \frac{(A - B) \times M \times K}{V}$$

- A = volume of sodium thiosulphate solution (B.1.5) required for the titration of the blank, in millilitres.
- B = volume of sodium thiosulphate solution (B.1.5) required for the titration of the sample, in millilitres.
- M = Molarity of the sodium thiosulphate solution (= 0.01).
- K = micro equivalent weight for sulphur dioxide = 32.030.
- V = sodium bisulphite stock solution taken, in millilitres.

The concentration of sulphur dioxide in the bisulphite standard solution (4.10) is found by dividing the result by 50.

ANNEX C

REMOVAL OF MERCURY FROM RESIDUAL SOLUTIONS

This Annex describes a method for the removal of mercury from the residual solutions received when using the absorbing solution (4.2).

C.1. Reagents

- C.1.1. Sodium hydroxide solution, approximately 400 g of NaOH per litre
- C.1.2. Hydrogen peroxide, H₂O₂, approximately 30 %, technical quality
- C.1.3. Sodium sulphide, Na₂S·9H₂O technical quality

C.2. Procedure

Collect in a polyethylene container with a volume of about 50 litres the residual solutions, whose mercury content is too high to allow them to be discarded through the sink. When the collected volume reaches approximately 40 litres, add in the following order, while stirring by means of air bubbling through the solution, a volume of sodium hydroxide solution (C.1.1) sufficient for neutralizing followed by 400 ml more. Add 100 g of sodium sulphide (C.1.3) and after 10 minutes, slowly 400 ml of hydrogen peroxide solution (C.1.2).

Leave the mixture for 24 hours and then draw off and discard the clear liquid. Transfer the residue to another container.

ANNEX D

PROPERTIES AND PURIFICATION OF PARAROSANILINE HYDROCHLORIDE

D.1. Test for the purity of the reagent

Dilute 1 ml of the PRA solution (4.4) to 100 ml with distilled water. Transfer 5 ml to a 50 ml volumetric flask and add 5 ml of a 0.1 M acetic acid-sodium acetate buffer solution. Dilute to the mark with water and mix.

Wait one hour and then measure the absorbance of the solution in a spectrophotometer at 540 nm in a 10 mm cell.

Calculate the concentration of pararosanine (PRA) as follows:

$$\% \text{ PRA} = \frac{\text{absorbance} \times K}{100 \text{ mg}}$$

where:

$$K = 21\,300.$$

If the purity of the pararosaniline is below 95 %, the reagent must be purified by one of the procedures described in D.2 and D.3.

D.2. Purification by extraction

In a 250 ml separatory funnel, equilibrate 100 ml each of 1-butanol and 1 M HCl. Weigh 0.1 g of pararosaniline hydrochloride (PRA) into a beaker. Add 50 ml of the equilibrated acid and let stand for several minutes. Add 50 ml of the equilibrated 1-butanol to a 125 ml separatory funnel. Transfer the acid solution containing the dye to the funnel and extract. The violet impurity will transfer to the organic phase. Transfer the lower (aqueous) phase into another separatory funnel and add 20 ml portions of 1-butanol. This is usually sufficient to remove almost all the violet impurity which contributes to the reagent blank. If the violet impurity still appears in the 1-butanol phase after five extractions, discard this batch of dye.

After the final extraction, filter the aqueous phase through a cotton plug into a 50 ml volumetric flask and bring to volume with 1 M HCl. This stock reagent will be yellowish red.

Note

Certain batches of 1-butanol contain oxidants that create a sulphur dioxide demand. Check by shaking 20 ml of 1-butanol with 5 ml of a 15 % potassium-iodide solution. If a yellow colour appears in the alcohol phase, redistill the 1-butanol from silver oxide.

D.3. Purification by recrystallization

Dissolve 1 g of pararosaniline hydrochloride in 250 ml of 2.5 M hydrochloric acid. Let the solution stand for two hours at room temperature. After filtration, the pararosaniline is reprecipitated by addition of a small excess of 2.5 M sodium hydroxide solution.

Collect the precipitate on a filter funnel (porosity 3). The filtrate should be colourless. Wash the precipitate with distilled water to remove excess sodium hydroxide and the sodium chloride formed.

Dissolve the precipitate in 70 ml of methanol heated to boiling and finally add 300 ml of water at 80 °C. Let the solution stand at room temperature. The pararosaniline reprecipitates slowly. The yield of recrystallization is about 64 %. Pararosaniline gets dark between 200 and 205 °C and decomposes at 285 °C.

Literature

H. G. C. King and U. G. Pruden: The determination of sulphur dioxide with rosaline dyes. *Analyst* 94, 43—48 (1969).