SECOND SUPPLEMENT TO THE GIBRALTAR GAZETTE

No. 2,860, of 10th August, 1995

PUBLIC HEALTH ACT

PUBLIC HEALTH (AIR QUALITY STANDARDS) RULES 1995

ARRANGEMENT OF RULES

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LEGAL NOTICE NO. 112 OF 1995

PUBLIC HEALTH ACT

PUBLIC HEALTH (AIR QUALITY STANDARDS) RULES 1995

In exercise of the powers conferred on him by section 337 of the Public Health Act, and of all other enabling powers, and for the purpose of transposing into the national law of Gibraltar Council Directives 80/779/EEC (as amended by Council Directive 89/427/EEC), 82/884/EEC, 85/203/EEC and 92/72/EEC, the Governor has made the following rules —

Title, commencement and application.

1. (1) These rules may be cited as the Public Health (Air Quality Standards) Rules l995 and shall come into force on the 1st day of September 1995.

(2) Rules 4 and 5 shall not apply to exposure to lead in the air as a result of a person’s occupation, and rules 6 and 7 shall not apply in relation to exposure to nitrogen dioxide in the atmosphere at work or within buildings.

Limit values for sulphur dioxide and suspended particulates in the atmosphere.

2. The Government shall take any appropriate measures to ensure that the concentrations of sulphur dioxide and suspended particulates in the atmosphere measured in accordance with rule 3 do not exceed the limit values set out in Schedule 1.

Measures of sulphur dioxide and suspended particulates.

3. (1) The Government shall ensure that measuring stations for measuring the concentrations of sulphur dioxide and suspended particulates in the atmosphere are established, and the concentration of sulphur dioxide and suspended particulates are measured in accordance with Schedule 2.

(2) The measuring stations shall be established at sites where pollution is thought to be greatest and where the measured concentrations are

representative of local conditions, and in particular in zones where the limit values referred to in rule 2 are likely to be approached or exceeded.

Limit value for lead in the atmosphere.

4. The Government shall take any necessary measure to ensure that the mean annual value for the concentration of lead in the air, measured in accordance with rule 5, does not exceed the limit value of 2 micrograms of lead per cubic metre expressed as an annual mean concentration.

Measurement of lead in the atmosphere.

5. (1) The Government shall ensure that sampling stations for measuring the concentration of lead in the air are installed and operated, and that the mean annual value is calculated in accordance with Schedule 3.

(2) The sampling stations shall be installed at sites where individuals may be exposed to lead in the air continually for a long period and where, in the opinion of the Government, the limit value referred to in rule 4 is likely to be exceeded.

Limit value for nitrogen dioxide in the atmosphere.

6. The Government shall take any necessary measures to ensure that throughout Gibraltar the concentration of nitrogen dioxide in the atmosphere measured in accordance with rule 7 does not exceed the limit value shown in Schedule 4.

Measurement of nitrogen dioxide in the atmosphere.

7. (1) The Government shall ensure that measuring stations for measuring the concentration of nitrogen dioxide in the atmosphere are established in accordance with Schedules 5 and 6.

(2) The measuring stations shall be established at sites selected in accordance with paragraphs l to 3 of Annex lll to Council Directive 85/203/EEC and in particular in zones where the limit value referred to in rule 6 is or is likely to be exceeded.

Measurement of ozone in atmosphere.

8. (1) The Government shall designate or establish measuring stations to supply the necessary data for the implementation of Council Directive 92/72/EEC on air pollution by ozone.

(2) The number and location of these stations shall be determined by the Government in accordance with Schedule 7.

(3) The Government shall ensure that at the measuring stations designated or established under sub-rule (1) concentrations of ozone in the ambient air are measured using either —

(a) the method set out in Schedule 8; or

(b) any other method of analysis shown to produce measurement results equivalent to those obtained using that method.

(4) Analysis for the purposes of sub-rule (3) shall be carried out by a laboratory designated by the Government for the purposes of Article 4 of Council Directive 92/72/EEC which may be one of laboratories designated by the Secretary of State under the Ozone Monitoring and Information Regulations l994.

(5) In the event of the values given in sub-rule (6) being exceeded, the Government shall take the necessary steps for the public to be informed in accordance with Article 5 of Council Directive 92/72/EEC and Schedule 9.

(6) The values referred to in sub-rule (5) are —

(a) the threshold for informing the public is l80µg/m^3 for the mean value over one hour;

(b) the threshold for issuing a public warning is 360µg/m^3 for the mean value over one hour.

Information.

9. In order that the Secretary of State may fulfill his obligations under —

(a) Article 7 of Council Directive 80/779/EEC (as amended by Council Directive 89/427/EEC);

(b) Article 5 of Council Directive 82/884/EEC;

(c) Article 7 of Council Directive 85/203/EEC;

(d) Articles 2 and 6 of Council Directive 92/72/EEC,

the Governor shall send to the Secretary of State such information obtained from the measurements taken under these rules as may be required by the Secretary of State.

SCHEDULE 1

Rule 2

LIMIT VALUES FOR SULPHUR DIOXIDE AND SUSPENDED PARTICULATES

(As measured by the black-smoke method)

TABLE A

LIMIT VALUES FOR SULPHUR EXPRESSED IN µg/m^3 WITH THE ASSOCIATED VALUES FOR SUSPENDED PARTICULATES (AS MEASURED BY THE BLACK-SMOKE METHOD (†) EXPRESSED IN µg/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)	=40 (median of daily mean values taken throughout the year)
Winter (1 October 31 March)	130 (median of daily mean values taken throughout the winter)	>60 (median of daily mean values taken throughout the winter)
	130 (median of daily mean values taken throughout the winter)	=60 (median of daily mean values taken throughout the winter)
Year (made up of units of measuring periods of 24 hours	250(*) (98 percentile of all daily mean values taken throughout the year)	>150 (98 percentile of all daily mean values taken throughout the year)
	350(*) (98 percentile of all daily mean values taken throughout the year)	=150 (98 percentile of all daily mean values taken throughout the year)

(†) 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 Part 1 of Schedule 2).

(*) Appropriate steps must be taken to ensure that this value is not exceeded for more than three consecutive days. If it exceeds three consecutive days it is a breach which the Secretary of State is obliged to report to the Commission. The Government shall 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 $\mu g/m^3$.

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 (Part 1 of Schedule 2).

(2) All appropriate steps must be taken to ensure that this value is not exceeded for more than three consecutive days. The Government shall endeavour to prevent and to reduce any such instances in which this value has been exceeded.

SCHEDULE 2

Rule 3(1)

PART 1

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 Part 2 of this Schedule, 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)/paraosaniline'. This method of analysis is based on the principle of the colorimetric reaction with paraosaniline.

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 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.

PART 2

REFERENCE METHOD OF ANALYSIS FOR SULPHUR DIOXIDE

AIR QUALITY - DETERMINATION OF THE MASS CONCENTRATION OF SULPHUR DIOXIDE IN AMBIENT AIR — TETRACHLOROMERCURATE (TCM)/PARAOSANILINE 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 $\mu g/m^3$ 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 paraosaniline containing phosphoric acid to obtain a pH of 1.6 ± 0.1.

Pararosaniline, formaldehyde and the bisulphite anion react to form the intensely coloured paraosaniline methyl sulphonic acid, which behaves as a two-colour indicator (Ámax =548nm at pH 1.6±0.1).

The concentration of sulphur dioxide is taken from a calibration graph prepared on the basis on 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 analysis).

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

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

Dissolve 10.9g of mercury (II) chloride, 4.7g of sodium chloride and 0.07g of ethylendiamine 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 60µg of iron (III), 10µg of manganese (II), 10µg of chromium (III), 10µg of copper (II) and 22µg 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 to this Schedule. 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 86ml of concentrated hydrochloric acid, HCl(p = 1.19 g/ml, to 1 litre.

4.4 Pararosaniline hydrochloride, 0.2% stock solution.

Dissolve 0.2g of paraosaniline hydrochloride, $C_{19} H_{17} N_3$ HCL in 100ml of hydrochloric acid (4.3).

Note 7

Paraosaniline hydrochloride used in the preparation of the stock solution must have a purity higher than 95% (see Annex D to this Schedule) and exhibit a maximum absorption at 540nm in acetic acid - sodium acetate buffer (0.1 moles/1). Furthermore, the absorbance of the reagent blank should not exceed 0.10 when the blank is prepared according to the procedure described in paragraph 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 to this Schedule).

4.5 Phosphoric acid, 3 moles/l.

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

4.6 Pararosaniline reagent solution.

Pipet 20ml of the pararosaniline hydrochloride stock solution (4.4) and 25ml of phosphoric acid (4.5) into a 250ml 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 0.6g of sulphamic acid, $NH_2 SO_3 H$, in 100ml water. This solution is stable for a few days if protected from air.

4.9 Sodium bisulphite solution. Stock solution.

Dissolve 0.3g of sodium metabisulphite, $Na_2 S_2 O_5$, in 500ml of freshly boiled and cooled distilled water (double-distilled water that has been deaerated is preferred). The solution contains from 320 to 400µg 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 to this Schedule).

The solution is unstable.

4.10 Sodium bisulphite standard solution.

Immediately after the standardization of the sodium bisulphite stock solution (4.9), pipet 2.0ml of the solution into a 100ml 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 5ºC. Stored at room temperature, it will be stable for one day only.

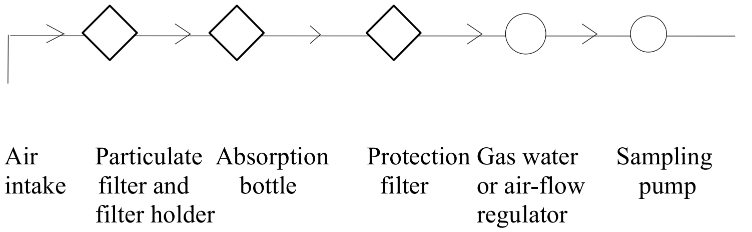
5. Apparatus.

5.1 Sampling equipment.

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

Figure 1

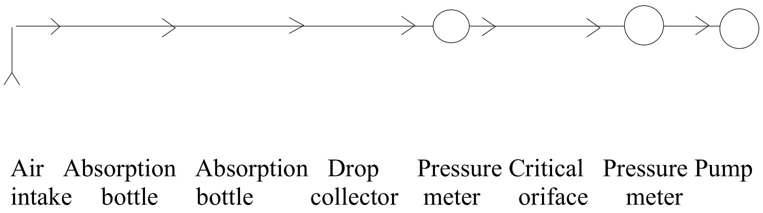
BLOCK DIAGRAM OF SAMPLING EQUIPMENT



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 to this Schedule.

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 midget impingers under the conditions described in paragraph 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 paragraph 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 Manometers

Two manometers accurate to 1000 Pa, for measurements of pressures when using a critical orifice instead of a gas meter.

5.6 Spectrophotometer or colorimeter.

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

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 10ml 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 aluminum foil, to prevent decomposition. The duration and flow rate of the aspiration depend on the concentration of sulphur dioxide in the air.

With midget impingers, the volume flow rate should be between 0.5l/min and 1l/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 3.0µg (0.2 to 1.2µl 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 the 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.

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

Prepare a blank by adding 10ml of unexposed absorbing solution (4.2) to a 25ml volumetric flask, add the reagents as described below and read the absorbance against distilled water using 10mm 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 decompositon 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 2ml of the formaldehyde solution (4.7) and 5ml 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 ±1.0) % 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 paragraph 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 determination 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 concentrations at reference conditions (25ºC, 1 bar) is needed, the volume of air sampled, V, must be replaced by the corresponding value of volume under reference conditions, V_R :

$$V_R - \frac{298V_P}{273 + T}$$

where

P = barometric pressure, in bar
T = Temperature of air sample, in °C.

7.2 Detection limit.

The detections limit of sulphur dioxide in 10 ml of TCM sampling solutions is between 0.2 and 1.0µg (based on twice the standard deviation). This corresponds to mass concentrations of sulphur dioxide of between 7 and 33 µg/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 17µg/m^3 at a concentration of 1 000µg/m^3 ([1]).

8. Literature.

8. (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, Swkl Project 21-2811. Environmental Protection Agency, Research Triangle Park, N.C., September 1971.

ANNEX A

ABSORBER MODELS

Muenke-flask **Midget impinger**

75 ml four holes, one
in bottom, each 1.5ø

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 12.7g of iodine, 1_2 , into a 250ml beaker, add 40g of potassium iodide, KI and 25ml of water. Stir until all is dissolved and transfer the solution quantitatively to a litre volumetric flask. Dilute to the mark with water.

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

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

B.1.3 *Starch indicator solution, 0.2%.*

Triturate 0.4g of soluble starch and 0.002g of mercury (II) iodide, HgI_2 (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 $Na_2S_2O_3H_2O$, in 1 litre of freshly boiled and distilled water and add 0.1g 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, $KI0_3$, 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

$$M - \frac{gKlO_3 \text{ x } 10^3 \text{ x } 0.1}{\text{ml sodium thiosulphate solution x } 35.67}$$

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 25ml of water to a 500 ml flask and pipet 50 ml of the iodine solution (B1.2) 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 (B1.5), 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):

$$SO_2\ (\mu g / ml)\ - \frac{(A - B) \times M \times K}{V}$$

A = volume of sodium thiosulphate solution (B1.5) 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 millitres.

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 400g of NaOH per litre.

C.1.2 Hydrogen peroxide, H_2O_2, approximately 30%, technical quality.

C.1.3 Sodium sulphide, $Na_2S.\ 9H_2O$ 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 solutions, a volume of sodium hydroxide solution (C.1.1) sufficient for neutralizing followed by 400 ml more. Add 100g 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 OR 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 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 pararosaniline (PRA) as follows —

$$\% \text{ PRA } - \frac{\text{absorbance x K}}{100 \text{ mg}}$$

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 D2 and D3.

D.2 Purification by extraction.

In a 250 ml separatory funnel, equilibrate 100 ml each of 1— butanol and 1 MHCl. Weigh 0.1g of paraosaniline 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 MHCl. 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 solution. If a yellow colour appears in the alchohol phase, redistill the 1-butanol from silver oxide.

D.3 Purification by recrystallization.

Dissolve 1 g of pararosaniline hydrochoride 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).

SCHEDULE 3

Rule 5(1)

CHARACTERISTICS TO BE COMPLIED WITH FOR CHOOSING A SAMPLING METHOD AND A REFERENCE METHOD FOR ANALYZING THE CONCENTRATION OF LEAD IN THE AIR

The atmospheric particles shall be collected on the filter of a sample for subsequent determination of lead content.

A. Characteristics to be complied with for choosing the sampling method.

Filter

1. The filter shall have a collection efficiency at the face velocity used in the sampling of not less than 99% for all particles of a mean aerodynamic diameter of 0.3µm.

Sampler efficiency

2.The sampler efficiency is defined as the ratio of the mass concentration in the atmosphere. The efficiency of a sampler may not be less than the values given in the following table an must be independent of wind direction.

Minimum acceptable efficiencies (%) for a sampler

Wind speed	*Particle size (aerodynamic diameter)*	
	5µm	10µm
2 ms^{-1}	95	65
4 ms^{-1}	95	60
6 ms^{-1}	85	40

Aspiration flow rate of sampling

3. The aspiration flow rate of sampling must remain constant to within ± 5% of the nominal value throughout a sampling period.

Location

4. As far as possible the sampling stations (or samplers) must be located in such a way as to be representative of the zones in which measurements must be made.

Operations

5.Sampling must be continuous although breaks of a few minutes each day or week are permissible to enable filters to be changed. An annual mean value will not be considered valid unless sampling has occurred on a minimum of 10 working days per month, during the first five years after the notification of the Directive and on a minimum of 15 working days per month thereafter, as far as possible, evenly spread over the period under consideration. The mean annual value is calculated by dividing the sum of the valid daily values by the number of days on which valid values have been obtained.

B. Reference method of analysis.

The reference method of analysis shall be atomic absorption spectrometry in which the analytical error for the determination of lead in the collected particles is less than a value corresponding to an atmospheric concentration of $0.1 \mu g m^{3}$ of lead (5% of the $\mu g m^{3}$ limit value). This analytical error should be maintained within the specified range by an appropriate calibration frequency.

SCHEDULE 4

Rule 6

LIMIT VALUE FOR NITROGEN DIOXIDE

(The value limit shall be expressed in $\mu g\ m^3$. The volume must be standardized at the following conditions of temperature and pressure: 293°C K and 101.3 kPa.)

Reference period (*)	Limit value for nitrogen dioxide
Year	200
	98th percentile calculated from the mean values per hour or per period of less than an hour recorded throughout the year(†)

(*) The annual reference period begins on 1 January in any given calendar year and ends on 31 December.

(†) To ensure that the validity of the calculation of the 98th percentile is recognized, 75% of the possible values must be available and, as far as possible, values must be available and, as far as possible, distributed uniformly throughout the year in question for that particular measurement site.

In cases where the values measured on certain sites are not available over a period exceeding 10 days, the calculated percentile must mention this fact.

The calculation of the 98th percentile on the basis of the values recorded throughout the year is to be carried out as follows — the 98th percentile must be calculated from the values actually measured. The measured values should be rounded off to the nearest $\mu g/m^3$. All the values are to be listed in increasing order for each site —

$$X_1 = X_2 = X_3 = \ldots\ldots\ldots\ldots = X_k = \ldots\ldots\ldots\ldots = X_{N-1} = X_N$$

The 98th percentile is the value of the component of rank K where K is calculated from the following formula —

$$k = (q \times N)$$

where q is equal to 0.98 for the 98th percentile and to 0.50 for the 50th percentile, N being the number of values actually measured. The value of (q x N) should be rounded off to the nearest whole number. Where measuring equipment does not yet allow the production of discrete values but provides only classes of values higher than 1 μgm^3, the member State concerned may, for the calculation of the percentile, use an interpolation, provided that the interpolation formula is accepted by the Commission and that the classes of values are not higher than 10$\mu g/m^3$. This temporary waiver is valid only for equipment currently installed for a time span not exceeding the life of the equipment and in any case limited to 10 years from the application of this Directive.

SCHEDULE 5

Rule 7(1)

REFERENCE METHOD OF ANALYSIS TO BE USED FOR THE PURPOSES OF THIS DIRECTIVE

1. The final reading of the instrument should be processed in such a way that an hourly mean or a mean of less than an hour may be calculated in accordance with provisions of Schedule 4. In order to enable possible checks to be made, data should be stored where —

— the limit value has not been exceeded, until the next periodic report by the Commission is drawn up as provided for in Article 8 of Council Directive 85/203/EEC,

— the limit value has been exceeded, until the measures called for in rule 7 have been taken.

The reference method of analysis to determine nitrogen oxides shall be the chemiluminescence method described in ISO standard DIS 7996.

For these methods the language versions published by the ISO and any other versions certified by the Commission as being in line with them shall be considered authentic.

In using the measurements methods, the following points should be taken into consideration —

a. The sampling head should be at a distance of at least 0,5 m from buildings in order to avoid a screening effect.

b. The sampling line (pipes and connections) should be inert materials (e.g. glass, PTFE, stainless steel) which do not alter the NO_2 concentration.

c. The sampling line between the samplings head and the instrument should be as short as possible. The time taken for gas volume samples to pass through the sampling line should not exceed 10 seconds.

d. The sampling head entry must be protected against rain and insects. If a pre-filter is used, it should be selected and maintained (regular cleaning) so as to minimize its influence on the NO_2 concentration.

e. Condensation in the sampling line must be avoided.

f. The sampling line should be cleaned regularly, taking local conditions into account.

g. Sampling should not be influenced by gas discharges from the instruments or discharges from the calibration system.

h. Sampling at the sampling head should not be influenced by adjoining installations (the air-conditioning or data transmission equipment).

i. All the necessary precautions must be taken to prevent temperature variations from producing an excessive percentage or errors of measurement.

j. The instruments should be calibrated regularly.

k. The sampling line must be air-tight and the flow-rate must be inspected regularly.

SCHEDULE 6

Rule 7(1)

MONITORING THE CONCENTRATION OF NITROGEN DIOXIDE

1. The purpose of measuring NO_2 concentrations in the environment is to assess the individual risk of exposure in excess of the limit value as closely as possible: measurement points should accordingly be chosen by the member States wherever possible from among sites where this risk is likely to be the greatest.

Two separate cases need to be considered —

1.1 zones predominantly affected by pollution from motor vehicles and therefore limited to the vicinity of roads carrying heavy traffic;

1.2 more extensive zones in which discharges from fixed sources also make a significant contribution to pollution.

2. In the case of 1.1, the measurement points should be selected so as to —

— cover examples of the main types of zone predominantly affected by pollution from motor vehicles, particularly ‘canyon’ streets carrying heavy traffic and major intersections,

— be, as far as possible, those in which NO_2 concentrations, as specified in paragraph 1, are likely to be among the highest.

3. The number of stations to be set up for the zones defined in paragraph 1.2 should reflect —

— the extent of the polluted zone,

— the uneven spatial distribution of the pollution.

The choice of sites should not exclude ‘canyon’ streets carrying heavy traffic and major intersections as defined in paragraph 2 if there is a danger of the limit value being exceeded owing to substantial pollution from fixed sources of combustion.

SCHEDULE 7

Rule 8(2)

PART 1

MONITORING OF OZONE CONCENTRATIONS

1. The purpose of measuring ozone concentration in ambient air to assess —

(i)as closely as possible the individual risk of exposure of human beings to values in excess of the health protection thresholds:

(ii)the exposure of vegetation (e.g. forests, natural ecosystems, crops, horticulture) to the values given in Annex 1 to this Part.

2. The measurement points must be located at geographically and climatologically representative sites where —

(i)the risk of approaching or exceeding the thresholds laid down in Annex 1 to this Part is the highest;

(ii)it is likely that one of the targets referred to in paragraph 1 is exposed.

At places where the member States do not have information concerning the sites referred to in (i) and (ii), they must carry out indicative measurement programmes in order to determine the siting of the measurement points to supply the data necessary for the implementation of this Directive.

3. Member States must establish or designate additional measurement points in order to —

(i)contribute towards the identification and description of the formation and transport of ozone and its precursors;

(ii)monitor changes in ozone concentrations in areas affected by background pollution.

Mandatory measurement of oxides of nitrogen and that recommended for volatile organic compounds be carried out in order to provide information on ozone formation, to monitor transboundary flows of volatile organic compounds and to make it possible to identify links between the different pollutants.

4. The final reading of the ozone measurement instruments must be carried out in such a way that the mean values over one hour and eight hours can be calculated, in accordance with the Annex to this Part and Part 2 of this Schedule.

ANNEX

THRESHOLDS FOR OZONE CONCENTRATIONS IN THE AIR(*)

(The values are expressed in µg03/m^3. The volume must be standardized at the following conditions of temperature and pressure 293 k and 101.3 kPa)

1. Health protection threshold.

110 µg/m^3 for the mean value over 8 hours (**)

2. Vegetation protection thresholds

200 µg/m^3 for the mean value over 1 hour

65 µg/m^3 for the mean value over 24 hours

3. The population information and moving thresholds mentioned in rule 8(6)(a) and (b).

(*) Concentrations must be measures continuously.

(**) The mean over 8 hours is a non-overlapping moving average; it is calculated 4 times a day from the 8 hourly values between 0 and 9.00, 8.00 and 17.00, 16.00 and 1.00, 12.00 and 21.00. For the information to be provided pursuant to Article 6 first indent of Council Directive 92/72/EEC, as required by rule 9, the mean over 8 hours is a simple moving average, calculated each hour h from the 8th hourly values between h and h-9.

PART 2

CALCULATION OF THE MEASUREMENT RESULTS FOR THE ANNUAL REFERENCE PERIOD

1. Concentrations must be measured continuously.

2. The annual reference period will begin on 1 January and end on 31 December in any given calendar year.

3. For the validity of the calculations of the percentiles (*) to be recognized, 75% of the possible values must be available and, as far as possible, distributed uniformly throughout the period in question for the particular measurements site. If that is not the case, this fact must be mentioned when the results are communicated.

* *the median must be calculated as the 50th percentile.*

The calculation of the 50th (98th) percentile on the basis of the values recorded throughout the year must be carried out as follows — the 50th (98th) percentile must be calculated from the values actually measured. The measured values must be rounded off to the nearest $\mu g/m^3$. All the values are to be listed in increasing order for each site —

$$X_1 = X_2 = X_3 = \ldots\ldots\ldots = X_k = \ldots\ldots\ldots = X_{N-1} = X_N$$

The 50th (98th) percentile is the value of k, to be calculated from the following formula —

$$k = 0{,}50(0{,}98)\cdot N$$

N being the number of values actually measured. The value of $0{,}50(0{,}98)\cdot N$ must be rounded off to the nearest whole number.

PART 3

INFORMATION TO THE PUBLIC

The following information must be circulated on a sufficiently large scale as soon as possible to enable the population concerned to take all appropriate preventive protective action. The information in question must be communicated to the media.

List of minimum details to be supplied to the public in the event of the occurrence of high ozone levels in the air —

1. Date, hour and place of the occurrence of concentrations in excess of the thresholds defined in paragraphs 1 and 2 of the Annex to Part 1 of this Schedule;

2. Reference to the type(s) of Community values exceeded (information or warning);

3. Forecasts — change in concentrations (improvement, stabilization or deterioration),

— geographical area concerned,
— duration;

4. Population concerned;

5. Precautions to be taken by the population concerned.

SCHEDULE 8

Rule 8(3)

REFERENCE METHOD OF ANALYSIS TO BE USED FOR THE PURPOSES OF THE DIRECTIVE

The reference method of analysis to be used in the context of this Directive to determine ozone is the UV absorption method. This method is being standardized by the ISO. Once the latter has published the standard in question, the method described therein will constitute the reference method in this Directive.

The following points must be taken into consideration when the measurement methods and instruments are used by the member States in the field —

1. the conformity of the operating characteristics of the measurement instrument with those indicated by the manufacture, in particular background noise, response time and linearity, must be verified initially in the laboratory and in the field;

2. this instrument must be totally calibrated regularly, using a reference UV photometer as recommended by the ISO;

3. in the field, the instruments must be calibrated regularly, e.g. every 23 or 25 hours; in addition, the validity of the calibration

must be verified by regularly operating in parallel an instrument calibrated in accordance with paragraph 1;

If the instrument inlet filter is changed before calibration, calibration must be carried out after an appropriate period of exposure (from 30 minutes to several hours) of the filter to ambient ozone concentrations;

4. the sampling head must be placed at least 1 m away from vertical screens in order to avoid any screening effect;

5. the sampling head opening must be protected against rain and insects.

   No prefilter is to be used;

6. sampling must not be influenced by adjoining installations (air conditioning or data-transmission equipment);

7. the sampling line must be of inert material (e.g. glass, PTEE, stainless steel) which is not affected by the presence of ozone. It must be exposed beforehand to appropriate ozone concentrations;

8. the sampling line between the sampling head and the analysis instrument must be as short as possible. In particular, the time taken for the gas volume sample to pass through the sampling line must be as short as possible (e.g. of the order of a few seconds in the presence of other reagents such as NO);

9. condensation in the sampling line must be avoided;

10. the sampling line must be cleaned regularly, taking local conditions into account;

11. the sampling line must be tight and the flow rate must be inspected regularly;

12. sampling must not be influenced by gas discharges from the instrument or from the calibration system;

13. all necessary precautions must be taken to prevent temperature variations from producing measurement errors.

SCHEDULE 9

Rule 8(5)

INFORMATION TO THE PUBLIC

The following information must be circulated on a sufficiently large scale as soon as possible to enable the population concerned to take all appropriate preventive protective action. The information in question must be communicated to the media.

List of minimum details to be supplied to the public in the event of the occurrence of high ozone levels in the air —

1. Date, hour and place of the occurrence in excess of the thresholds defined in paragraph 3 of the Annex to Part 1 of Schedule 7 and rule 8(6)(a) and (b);

2. Reference to the type(s) of Community values exceeded (information or warning);

3. Forecasts — change in concentrations (improvement, stabilization or deterioration);

   — geographical area concerned,
   — duration;

4. Population concerned;

5. Precautions to be taken by the population concerned.

Dated this 10th day of August 1995.

By Command,

M. J. Robinson,

Deputy Governor.

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