D. JOHNSON

SHORT AND LONG TERM METHODS FOR AIR SAMPLING IN AIR QUALITY CONTROL

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INDEX

3.2.1 Manual Methods

(a) Intersociety Committee
(b) U.S. E.P.A. Method 6
(c) U.S. E.P.A. Method 8
(d) C.E.R.L.
(e) British Standard
(f) N.S.W. Clean Air Act Regulation

4 Sulphur Dioxide

4.1 Ambient Levels

4.1.1 Manual Methods

(a) British Standard
(b) Colourimetric

4.1.2 Automatic Methods

(a) Conductometric
(b) Colourimetric
(c) Coulometric
(d) Solid Electrolyte Membrane
(e) Pulsed Fluorescence
(f) Flame Photometry
(g) Second Derivative Spectroscopy
(h) Remote U.V. Detection

4.2 Source Levels

4.2.1 Manual Methods

(a) Intersociety Committee
(b) U.S. E.P.A. Method 6
(c) U.S. E.P.A. Method 8
(d) C.E.R.L.
(e) British Standard
(f) N.S.W. Regulation
(g) Detector Tubes
(h) Canadian E.P.S.

4.2.2 Automatic Methods

(a) NDIR
(b) Solid Electrolyte Membrane
(c) U.V. Pulsed Fluorescence
(d) Flame Photometry
(e) Second Derivative Spectrometry
(f) Remote U.V. Detection

5 Carbon Monoxide

5.1 Ambient Levels

5.1.1 Manual Methods

(a) Gas Detector Tube

5.1.2 Automatic Methods

(a) NDIR
(b) Hopcalite
(c) Electrochemical

5.2 Source Levels

5.2.1 Manual Methods

(a) Absorption
(b) Combustion
(c) Gas Detector Tube

5.2.2 Automatic Methods

(a) NDIR
(b) Catalytic Combustion

6 Nitrogen Oxides

6.1 Ambient Levels

6.1.1 Manual Methods

(a) Saltzmann
(b) Jacobs - Hochheiser
(c) Gas Detector Tubes

6.1.2 Automatic Methods

(a) Colourimetric
(b) Coulometry
(c) Chemiluminescence
(d) Solid Electrolyte Membrane
(e) Remote U.V. Detection
(f) Second Derivative Spectroscopy

6.2 Source Levels

6.2.1 Manual Methods

(a) Colourimetric
(b) Gas Detector Tubes

6.2.2 Automatic Methods

(a) NDIR
(b) Second Derivative Spectrometry
(c) Chemiluminescence
(d) Solid Electrolyte Membrane
(e) Remote U.V. Detection
(f) Second Derivative

7 Hydrocarbons

7.1 Ambient Levels

7.1.2 Automatic Methods

(a) HFID
(b) C_2-C_5 Hydrocarbons
(c) High Molecular Weight Hydrocarbons
(d) Mass Spectrometer
(e) Infra Red Spectrometer

7.2 Source Levels

7.2.1 Manual Methods

(a) Gas Detector Tubes

7 2.2 Automatic Methods

(a) NDIR
(b) Gas Chromatography
(c) FID

10.2.2 Automatic Methods

(a) Flame Photometry

11 Ozone

11.1 Ambient Levels

11.1.1 Manual Methods

(a) Colourimetric

11.1.2 Automatic Methods

(a) Colourimetric
(b) Coulometry
(c) Chemiluminescence
(d) U.V. Absorption

11.2 Source Levels

12 Chlorine

12.1 Ambient Levels

12.1.1 Manual Methods

(a) O-Tolidine
(b) Methyl Orange
(c) Iodine Thio Sulphate

12.1.2 Automatic Methods

12.2 Source Levels

12.2.1 Manual Methods

(a) O-Tolidine
(b) Methyl Orange
(c) Iodine Thio Sulphate

13 Carbon Dioxide

13.2 Source Levels

13.2.1 Manual Methods

(a) U.S. E.P.A.
(b) Canadian E.P.S.
(c) South Australian Clean Air Act

13.2.2 Automatic Methods

(a) NDIR

14 Hydrogen Chloride

14.1 Ambient Levels.

14.2 Source Levels

14.2.1 Manual Methods

(a) Gas Detector Tubes
(b) Potentiometric Titration
(c) Turbidimetric
(d) Titrimetric
(e) N.S.W. Regulation

14.2.2 Automatic Methods

(a) NDIR

15 Aldehydes

15.1 Ambient Levels

15.1.1 Manual Methods

(a) M.B.T.H.

15.1.2 Automatic Methods

15.2 Source Levels

15.2.1 Manual Methods

(a) M.B.T.H.
(b) Bisulphite Absorption
(c) Colourimetric

15.2.2 Automatic Methods

(a) FID

16 Odour

16.1 Ambient Levels

16.1.1 Manual Methods

(a) Human Nose
(b) Gas Chromatography

16.1.2 Automatic Methods

16.2 Source Levels

16.2.1 Manual Methods

16.2.2 Automatic Methods

17 PAN

17.1 Ambient Levels

17.1.1 Manual Methods

(a) Hydrolysis
(b) Gas Chromatographic
(c) Infra Red Spectroscopy
(d) Elemental Analysis

17.1.2 Automatic Methods

17.2 Source Levels

INTRODUCTION

This paper contains most of the methods of air pollution sampling and analysis in use today. An earlier paper by Ferrari (see Ref 1) covered the automatic measurement of pollutants in the ambient atmosphere, but here it is intended to increase the field of measurement to encompass both source and ambient levels and to give adequate references for those who require indepth knowledge on the subject. Though the method of sampling for source concentrations relate mainly to stationary situations the methods of analysis in general also apply to pollutants from the automobile.

The pollutants discussed include particulates as suspended, deposited and metallic also sulphur trioxide, sulphur dioxide, carbon monoxide nitric oxide, nitrogen dioxide, hydrocarbons, fluorides, hydrogen sulphide, mercaptons, ozone, chlorine, carbon dioxide, hydrogen chloride, aldehydes, odours and PAN. Common sources for each pollutant are given and then manual and automatic methods for both ambient and source levels are discussed. Comments where appropriate are made on advantages and disadvantages of the method.

The philosophy of manual batch methods versus continuous automatic methods for the estimation of pollutant levels in recent times has become more clear cut with a preference to the latter.

In general manual methods have a reasonable amount of specificity for the pollutant in question, have a low to average sensitivity and can only give an integrated value over the sample period. The cost of the sampling apparatus is relatively cheap and the analysis is carried out with instruments that are frequently found in an analytical laboratory. However, analysis has to be performed on each individual sample and the labour cost involved in the collection and analysis of the sample can be considerable.

Automatic continuous measurement in many cases has progressed through the first generation of instrumentation which carried out the analytical chemistry of the manual methods, automatically. This period, in retrospect, was not very satisfactory as it frequently relied on reactions which were slow, insensitive, non-specific and reagents which were unstable and bulky. There was a considerable effort required to keep the instruments in service-maintaining reagents, liquid pumps, air pumps and numerous plumbing fittings. The accuracy of measurement relied on maintaining the ratio of the sample air to the reagent flow. Current automatic instrumentation is a vast improvement and is generally highly specific, very sensitive and tends to rely on gas phase reactions or a physical measurement in the gas phase. (See Ref. 2) Some of these methods like nondispersive infra red (N.D.I.R.), pulsed fluorescence, second derivative, nephelometry and opacity rely on a fixed sample path without the need to critically control the sample flow. This freedom significantly increases the potential long term accuracy of measurement. Automatic instruments give a continuous readout of levels measured which can be stores on a stripchart or computer tape. Their initial cost is high and they are dedicated instruments but they give continuous measurements at a lower cost per reading.

2/...

While the area of automatic measurement of pollutant levels in the air has been developing over the last two decades it is only recently that this trend has moved into the source or emission field. The testing of emissions from stationary sources has changed radically over the last 5 years. This change has been brought about largely because of the need for the continuous measurement of pollutants being emitted from these sources. Traditionally these emissions have been measured by taking a "batch" sample from the chimney or emission point, dissolving or reacting it in some suitable liquid phase and returning it to the laboratory for analysis. It is obvious that this type of testing gives results which could be, and in many cases, are, non-typical. This occurs for many reasons:- the process being measured may be cyclic or at least non uniform or the control equipment being tested can either be tuned above normal efficiency or the load on the plant reduced for the duration of the test. Instead of taking a "grab" sample of a few cubic metres of stack gas, these new instruments make it possible to monitor emissions for periods of days or weeks. It allows for measurement in periods such as the middle of the night when many people feel that factories have their highest emissions.

The advantages of this type of monitor to a control agency are obvious. But it is also of advantage to the supervising staff of the factories. They are then made aware, by checking the instrumen readout, when the emissions from the plant are over an emission limit and can take corrective action before the situation deteriorates further. It also gives them a check of operations on night shift when supervision is limited.

The Environmental Protection Agency of the United States of America (E.P.A.) have recently made it mandatory for large installations to continuously monitor their emission (see Ref. 3). These include fossil fuel-fired steam generators, nitric acid plants, sulphuric acid plants and fluid bed catalytic cracking unit catalyst regenerators at petroleum refineries. The parameters to be measured include opacity, sulphur dioxide, oxygen and oxides of nitrogen; the particular parameter or parameters to be measured depending on the type of plant. The results of the monitoring are to be returned to the E.P.A. for analysis and, in spite of the Fifth Amendment could be used to prosecute the companies.

3/...

1. PARTICULATES

Particulates can be defined as any dispersed matter, solid or liqui in which the individual aggregates are larger than single small molecules (about 0.0002um in diameter) but smaller than about 500um (see Ref. 4). However a better working definition may be solid particles of size greater than 0.01um.

Particulate pollution in the atmosphere may be classified into two arbitrary groups, based on methods of measurement.

(a) Solid material such as grit which is large enough to be deposited on the ground by the action of gravity. Particl in this category are larger than 10 to 12um and are common measured using a dust deposit gauge or high volume sampler

(b) Finer material such as smoke and aerosols which remain suspended in the air by Brownian movement. Particles in this category range up to 10um and are measured using coefficient of haze measurement, nephelometry or the British Standard method.

Sources:-

The actual sources of atmospheric particulates are legion. Excludin natural precipitation of water vapour, particles can arise from combustion of fossil fuel, condensation, volcanic eruption, break down of larger particles in the atmosphere, pulverization of road dust by vehicles, tyre wear, wind erosion, soil, process dusts, sea-salt and photochemical reactions.

1.1 Ambient Levels

1.1.1 Manual Methods

(a) Dust Deposit Gauge (See Ref. 5 and 6

A deposit gauge normally used in Australia is similar to a rain gauge, and consists of a 150mm diameter funnel supported inside the neck of a 2 litre bottle. During the period of exposure, usually 30 days, particles are deposited into the bottle via the funnel. The bottle is placed in a stand approximately 1½ metres above ground level.

Following exposure the insoluable deposited matter is estimated gravimetrically and then ashed. The results are expressed as a dust deposition rate in mass per unit area per month.

A detailed method of analysis of the deposit gauge sample is discussed in British Standard 1747 Part 1. The Australian gauge is somewhat different to the gauge described in the British Standard. Typical levels measured usually fall in the range 0.5-20g/m^2/month.

Another gauge occasionally used is a directional deposit gauge and it is used to access the source of deposited matter in terms of wind direction. It has four cylindrical containers, slotted vertically spaced at 90^o intervals to each other and suspended 1-2 metres above ground level. The gauge is aligned to collect pollution from the four points of the compass.

Comments. The results from a deposit gauge are not a very accurate measure of dust deposition and are very dependant on meteorological a seasonal fluctuation. The main advantage of the device is that it is inexpensive.

(b) High Volume Sampler (See Ref. 7 and 8)

A high volume sampler is used to collect the smaller particles of deposited dust and suspended matter on a glass fibre filter paper in the size range from 0.1 to 100um.

Air is drawn into the covered housing and through a 500cm^2 glass fibre filter paper at a flow rate of approximately 1.7m^3/min. The filter paper lies horizontally and the covered housing protects the filter from direct fallout and rain. The air sample is drawn around the housing and onto the filter paper. A sample is taken over a continuous 24 hour period (midnight to midnight). Samples are normally taken at intervals of 6 days.

The mass concentration of sample collected in the ambient air is determined gravimetrically and knowing the total volume of air sampled, the concentration is expressed as ug/m^3. Typical ranges measured using this technique are 20 to 500ug/m^3. In areas where fallout significantly exceeds 500ug/m^3 an 8 or 12 hour sample can be taken.

Comments. A relatively inexpensive device but it needs manual changing of filter.

(c) British Standard Method (See Ref. 9)

This and the following two methods measure particles in the size range 0.1 to 10-12um.

A continuous air sample is drawn through a No. 1 Whatman filter held between a filter holder. The usual diameter of the filter is 2.54cm. The flow rate is 1.5 litres per minute and the sample is taken over 24 hours. The soil on the filter paper is then determined by comparing the light reflectance of the stain to the light reflectance from the blank filter. Using this reflectance the surface concentration is determined from the O.E.C.D. International Curve (B.S. 1747 Pt. 2 p11) from which the concentration, expressed in ug/m^3, is determined by calculation.

It must be remembered that levels recorded using this technique are only arbitrary. Due to the physical nature of the particles which are being measured, for example opacity and size, absolute measurement is not possible.

Typical levels which may be measured using this method range between 10 and 200ug/m^3. If measurements are required in regions where levels lie outside this range then a smaller (1.27cm) or larger (5.08cm) filter holder should be used.

Comments: It only gives a once daily integrated reading but the results can be compared with World Health Organisation (WHO) goals.

1.1.2 Automatic Methods

(a) Paper Tape Sampler (Coefficient of Haze) (See Ref. 10)

By means of a vacuum pump, ambient air is automatically drawn at a flow rate of 7 litres per minute, for a period of 2 hours through a sampling nozle that clamps and shrouds a No. 4 Whatman filter paper tape. However, on most commercially available instruments this sampling period is variable from 10 minutes to 3 hours or longer. Suspended matter in the air is filtered on the tape through a 2.54cm diameter spot. After each sample is taken the filter tape is automatically positioned to a fresh section and sampling continues.

Samples so collected are measured by comparing the light transmission through the filter stain to that transmitted through the blank tape. Using the optical density obtained from the transmission reading and knowing the number of linear feet of air sampled, the level of suspended matter is calculated and expressed as a Coefficient of Haze (COH). Again, as discussed in Section 1.1.1 (c) this is only an arbitrary value and in this case it is not expressed as a concentration.

Using two hour sampling periods, most instruments are designed to operate unattended for up to six weeks. Some instruments automatically sample, measure and record the readings. Coefficient haze units range between 0 to 10.

Comments: More flexible than the previous method but the results cannot be related directly to WHO goals.

(b) Nephelometry (See Ref. 11 and 12)

The light scattering ability of aerosols provides the basis for a continuous measurement of suspended matter in the atmosphere.

One commercial method available draws a continuous air sample at approximately 300 litres per minute through a sample cell where it is then subjected to pulsed light from a xenon lamp. The resulting scattered light due to the interference caused by the particles is detected using a light sensitive photomultiplier tube which is shielded from direct exposure from the xenon light source. The signal produced by the photomultiplier tube is averaged and compared to the reference voltage of a second photomultiplier tube which looks at the total intensity of the xenon light.

For a given particle size of a known material there is an accurate relationship between the mass of the sample loadings and the scattered light. However, this correlation decreases in the practical measurement of suspended matter due to the heterogeneous nature of the size and type of particles in the ambient air.

Humidity severely effects this type of measurement although the interference is greatly reduced by preheating the air sample during its passage through the sampling line. Aerosol "Freons" are quite commonly used as a satisfactory means of calibrating nephelometers.

6/...

Comments: This is the only method which gives a continuous readout of the concentrations of particles in the atmosphere. It also assesses visual distance.

(c) Low Energy Beta Absorption (See Ref. 13)

The principle of using beta radiation for measuring suspended matter levels is claimed to be independent of the chemical composition or physical properties of particles in the size range 0.3 to 5 um.

The method requires that a known volume of ambient air be drawn through a filter paper (similar to a paper tape sampler) and the mass collected determined by the absorption of low energy beta radiation following its passage through the sample. The radiation absorbed is proportional only to the mass of sample collected on the filter paper and is independent of both its density or chemical composition, and physical or optical properties. Knowing both the volume of air sampled and the mass of sample collected then the result can be expressed as an absolute concentration in ug/m^3.

One commercially available instrument has a range of sampling time from 10 minutes to 12 hours. For a one hour sampling period the measuring range is between 10 to 200 ug/m^3.

Comments. It gives a direct mass concentration readout but only as integrated readings.

1.2 Source Levels

1.2.1 Manual Methods

Most manual methods are based essentially on the same principal. Particulate matter is withdrawn isokinetically from the source and its mass determined gravimetrically after the removal of uncombined water. Isokinetic sampling is necessary because particulates do not behave as ideal gases and are not homogenously mixed in the exhaust stream and precautions have to be taken to achieve a representative sample.

In isokinetic sampling the velocity of the gas entering the sample nozzle is adjusted as near as possible to the velocity of the gas in the stack at that sampling point. If the velocity into the nozzle does not equal the velocity in the stack, the sample will be biased due to the behaviour of the different sized particles entrained in the gas stream. For example, if the velocity through the nozzle is greater than in the stack, smaller particles will tend to be over-represented due to the fact that they are more easily able to follow the flow lines. For velocities lower though the nozzle, larger particles will be over-represented for similar reasons. Note that the assumption is made that particles are travelling at the same velocity as the stack gas.

7/...

Velocity of gas in a stack can vary quite considerably from point to point in cross section. as can the particulate concentration. It is therefore necessary to choose a number of sampling points, the actual number and position depending on the size and geometry of the stack. (See Ref. 14, 15 and 16).

To perform an emission test for particulates, the velocity profile of the stack must be known. This is normally determined by measurement of the velocity by a Pitot tube or in some instance by a mass flow meter. The velocity is measured at a number of points, predetermined as above, the gas is then withdrawn isokinetically from the stack and the particulates separated by a filtration step. The filtered particles are then dried and weighed and the concentration expressed as grams per cubic metre. Cubic metre being defined as that volume of dry gas which occupies a cubic metre at STP. For incinerators and boilers, the concentration is usually corrected to 12% carbon dioxide to allow for uniform combustion, this requiring the concurrent measurement of Carbon Dioxide during the test.

Isokinetic methods for sampling particles all follow this broad principal, but differ in the method of filtration and volume measurement.

(a) U.S. E.P.A. Method 5 (See Ref. 17,18 and 19)

This is becoming the method most used throughout the world. The velocity distribution is determined during the sampling traverse. The sample is drawn through the sampling train as follows. The dust is separated from the gas stream by an external (to the stack) heated filter (99.7% efficient for 0.3 um). An external cyclone for separation of the particulates is optional and if used, precedes the filter. This is followed by an impinger train consisting of 1 Greenburg-Smith and 3 modified Greenburg-Smith impingers to cool the gas. remove any residual particles, a dry trap for liquid removal and a silica gel trap for moisture removal. The gas then runs to a pump, and a dry gas meter, an orifice gauge and a thermometer. For this method the moisture content and the molecular weight of the stack gas are to be measured and included in the calculations. Velocity is determined by an S-type Pitot, and stack temperature is measured with a thermocouple.

Comments: The method can only be used for vertical stacks and the sample is collected in two or three separate zones making it somewhat tedious for analysis.

(b) Canadian E.P.S. Method (See Ref. 20)

This is very similar to the U.S.E.P.A. method 5, except that a cyclone is mandatory before the filter. and the thermocouple is to be included in the S - type Pitot.

Comments: As for (a) above.

8/...

(c) Joy WP - 50 Particulate Train (see Ref. 21)

This method uses in-stack filtration with the filtering medium, usually an alundum thimble, placed right after the nozzle. This followed by a wet collector, a total volume gas meter and thermometer and a pump, but no flow rate measurement.

Comments: In-stack filtration is considered an advantage but the lack of a flow rate device means delays in attaining isokinetic rates at each point.

(d) Los Angeles County Air Pollution Control District Particulate Train (See Ref 22)

There are three methods developed by the APCD. For hot gases, an external ceramic filter is used to collect the dust followed by a wet collector. For gases of lower temperature, a paper thimble is used For incinerators a collection head is used which also sizes the particulates collected. The gas conditions are measured by a thermometer, total volume meter, and a pump with no flow rate measurement.

Comments: The flexibility makes the method practical, but no flow rate measurement is a handicap.

(e) A.S.T.M. Particulate Train (See Ref 23)

This method is very similar to the Joy train except there is a flow rate measuring ability and the filtering medium is flexible, depending on the type of particulate to be collected.

Comments: A practical method.

(f) A.S.M.E. Particulate Train (See Ref. 24)

This lays down a list of specifications such as nozzle type, filtering medium, velocity measurement, volume measurement and pump system; most methods meet these specifications.

(g) San Francisco County Air Pollution Control District (See Ref. 25)

This method uses in - stack filtering, with the nozzle and filter holders being made of Pyrex and the filter made of glass wool.

Comments: In - stack filtration is considered an advantage but the pyrex nozzle and filter holders are fragile.

(h) British Standard Methods (See Ref. 15)

British Standard 3405:1961 details a number of methods for dust emission testing based on in - stack filtering with thimbles or cyclones. Flow rate measurement is done with an orifice gauge and volume measurement by measuring flow and time.

Comments: Practical.

9/...

(i) N.S.W. Clean Air Act Regulation Method (See Ref. 16)

This method is based on BS 3405:1961, but with many modifications. It is probably the most flexible method allowing for heated or non-heated probes, many types of filtering medium (normally in - stack) and has the ability to be used on vertical or horizontal ducts.

Comments: The flexibility makes it very practical.

(j) American Petroleum Institute Filtration Method (See Ref. 26)

In this method, the gas is sampled at only one point. The filtration is in - stack using paper or glasscloth filters, and the gas volume is by gas meter. There is no flow measuring device. and pitot readings are taken before the test.

Comment: Sampling in one position make the method rather inaccurate.

(k) American Petroleum Institute Impingement Method (See Ref. 27)

This method is very similar to the Filtration method, but uses impingers instead of thimbles for dust collection.

Comments: As for (j) above.

(l) American Petroleum Institute Impaction Method (See Ref. 28)

This method uses a Cascade impactor to collect particles. The Cascade Impactor consists of 4 jets with glass slides below the tips. The jets are at right angles to each other and the slides are tared and microscopically clean. The velocity through the jets increases as the gas moves on and particles between 200 um and 0.1um can be collected. The sampling system is similar to the other API methods.

Comments: Rather limited in application but gives a separation in terms of particle size range.

(m) Bacharach Test (See Ref. 16)

This is a method for testing the emissions from oil or gas fired equipment. The exhaust gas is drawn from the stack with a hand pump of standard bore through a filter paper and after 10 strokes the soiled spot on this paper is compared to standards spots. The standard spots are numbered 1 white, to 10 black.

Comments: This is not an isokinetic measurement and results do not relate to other methods. The simple apparatus enables rapid testing and immediate readout.

(n) Ringelmann Chart (See Ref. 16)

This is a method to visually access the intensity of smoke coming from an emission point. The chart is a series of 5 panels graded number 1 to 5. with black hatching on a white background. Each ascending number represents a 20% increase in blackness. To take a reading the observer stands 30 to 50 metres behind the chart and aligns it with the point of emission. The Ringelmann number approaching the shade of the smoke when viewed in this fashion is the rating. A miniature ringelmann chart is also available

10/...

Comments: This is a remote test and enables a simple rapid result. It is non isokinetic, subjective and the results do not relate to other methods. It can only be used in daylight.

For more detailed information on methods of testing for particulate emissions see Ref. 29.

1.2.2 Automatic Methods

(a) Opacity Meters (see Ref. 30)

Opacity meters rely on the principle of shining a light across a stack and measuring the reduction in light received at the other side. There is a great variation in the sophistication of different instruments of this class ranging from the simple smoke alarm to the very sophisticated on stack transmitometer. These latter instruments have selected wavelength light to reduce interference, narrow angle of beam acceptance to reduce effects of scattered light, chopped sample and reference beams to reduce stray light interference, self cleaning optics and in built calibration and zero checks. The instrument can be calibrated to read directly in emission concentration by performing manual emission tests and relating this to the opacity measurements.

Comments: It is not an isokinetic method and water droplets interfere. Its advantages are that it provides in stack measurement which averages the total cross section of the emission. It provides a continuous readout.

(b) Beta Ray Attenuation (See Ref. 13 31, and 32)

This principle relies on the sequential sampling of particles from the stack onto a tape and then bombarding the soiled spot with high velocity electrons. The absorption of electrons by the particles, is compared with the absorption on a fresh tape and the attenuation is proportional to the mass of particles collected. This method is not strictly continuous but gives a series of integrated readings over a time period. Generally the sampling is in one spot of the stack and is not strictly isokinetic.

Comment: It is not isokinetic but gives a mass concentration readout. It is not a continuous method.

11/...

2. METALS

Measurement of pollution by fumes or particles of metals is usually confined to the more common toxic elements such as lead, arsenic, antimony, cadmium, mercury or any of their compounds (see Ref. 5). However, the method of sampling for any metallic element is essentially the same, the method of analysis being the major difference.

Sources:

Particles and fumes come from a diverse number of sources. Lead comes largely from motor vehicle exhausts, usually in the form of lead halide, while lead smelting, refining and mining are other large contributors. Mercury is emitted by chlor-alkali plants and is used widely as a fingicide. Other metals in the atmosphere owe their origin mainly to either smelting, refining or mining of the respective metals and their compounds.

2.1 Ambient Levels

2.1.1 Manual Methods

Metal particles are routinely collected from the atmosphere by high volume sampling (See 1.1.1(b)) and in specific cases by low volume sampling. However, there are a number of methods of analysis which differ quite markedly from each other.

For mercury, high volume sampling is not normally used. There are methods published on these alternate procedures (See Ref.33 and 34).

Analysis

(a) Canadian E.P.S. Method (See Ref 35)

In this method a portion of the filter is cut out with a wad punch and the portion dissolved in hydrofluoric acid. The resultant solution is dried, nitric acid added, filtered and diluted. This solution is then analysed by atomic absorption spectrophotometry.

(b) Intersociety Method (See Ref. 36)

This method involves the use of a low temperature asher. A portion is cut from the filter and ashed at 150°C (250 watts, 1 mm. chamber pressure, 50 cc per minute oxygen). The ashed filter is extracted with Hydrochloric/nitric acid, then concentrated, diluted, centrifuged and analysed by atomic absorption. It is a very long method.

(c) Extractive Methods (See Ref. 37 and 38)

Extractive methods involve the direct extraction of metal particulates into acid, either nitric, nitric/perchloric or nitric/hydrochloric. They generally have an initial dry ashing, the temperature depending on the metal or metals being analysed. The final solution is analysed by atomic absorption.

12/...

(d) Non-Destructive Methods

This type of method involves the direct measurement of the metal content of the sampled particulates. A number of methods are used, the most popular being X-Ray florescence. However, to use these methods, low volume sampling must be employed, using a membrane type filter. This is necessary because the dust must be on the surface of the filter. Calibration is also difficult using these methods.

2.2 Source Levels

2.2.1 Manual Methods

There are no commercially available instruments specifically for the sampling of emissions of metals. However, any of the isokinetic particulate test methods could be used, and the particulates analysed for metal content by atomic absorption spectrocopy. Alternatively, the filtering medium on the isokinetic test equipment can be removed and the sampling train consisting of the probe and impingers of dilute nitric acid used. The acid in the impingers both removes and dissolves the metals from the gas stream. (See Ref. 19).

Mercury is a separate case and a number of methods have been published for the collection and analysis of mercury from stationary sources (See Ref. 144). These involve either:-

(i) Absorption by aqueous iodine monochloride;
(ii) Absorption by Potassium Permanganate;
(iii) Amalgamation with Silver or Gold;
(iv) Adsorption by charcoal.

3. SULPHUR TRIOXIDE AND SULPHURIC ACID MIST

Sources:-

The majority of sulphur oxides in the atmosphere come from the combustion of the sulphur contained in fossil fuels. Between 90-100% of this sulphur is emitted as Sulphur Dioxide, but depending on the combustion conditions, oxidation must go further to form Sulphur Trioxide. This can be emitted as Sulphur Trioxide or Sulphuric acid mist, depending on the temperature of emission, but will become mist shortly after emission into the atmosphere. Other sources of Sulphur Trioxide are Sulphuric Acid Plants, Smelters, processes using sulphur or sulphuric acid and Petroleum refining.

3.1 Ambient Levels

At this time there are no methods specifically designed for the measurement of sulphur trioxide in the atmosphere.

3.2 Source Levels

3.2.1 Manual Methods

Manual methods are based on two principles. Firstly the Sulphur Trioxide is separated from the gas stream by selective condensation and in the second method, the sulphur trioxide is absorbed in a liquid medium, 80% Iso-propyl alcohol, which inhibits the oxidation of any sulphur dioxide absorbed. Note that manual methods also involve the simultaneous estimation of Sulphur Dioxide.

(a) Intersociety Committee on Methods of Air Sampling and Analysis (See Ref. 39, 40 and 41)

Flue gas is drawn from the stack, non-isokinetically, through a heated filter (to remove particulate matter) then through a heated glass probe (to prevent condensation and reaction). In the resultant gas stream, sulphur trioxide is condensed as sulphuric acid by controlled cooling and the resulting aerosol is collected on a glass frit filter. The sulphuric acid is then washed off and determined by reaction with Barium Chloronilate and measurement of the coloured complex on a spectrophotometer at 530 nm. Alternatively the sulphate can be determined by alkali titration with Barium Perchlorate using thorin indicator. The volume sampled is measured with a gas meter.

Comments

In some situations, like sampling from glass tanks, fine particulates can cause frequent blocking of the filter. Non-isokinetic sampling could cause inaccurate results if the compound is present as a mist.

(b) U.S. E.P.A. Method 6 (See Ref. 4, 17 and 18)

This method is primarily for the determination of sulphur dioxide from stationary sources, but since it also involves the separation of Sulphur Trioxide, it could be used as a method of analysis. Gas is proportionally drawn from the stack, through a heated probe with a glass wool filter, into a bubber of 80% Isopropyl Alcohol, at a flow rate of approximately 3 litres per minute. Analysis is performed by titration with Barium Perchlorate against thorin. Total volume is measured with a gas meter.

Comments

For the sampling of sulphuric acid nist, the method suffers because it is not isokinetic. Also any sulphur dioxide dissolved in the isopropanol would have to be allowed for.

(c) U.S.E.P.A. Method 8 (See Ref. 4, 17, 18 and 19)

This method is specifically for the determination of sulphur trioxide and sulphuric acid mist from sulphuric acid plants. A gas sample is withdrawn isokinetically from the stack through a heated probe into an impinger of 80% Isopropyl Alcohol at a flow rate of approximately 30 lites per minute. This is followed by a fibreglass filter (MSA type 1106 BH or equivalent) which entrains sulphuric acid mist. The filter is added to the solution and the mix analysed for sulphate by titration with Barium Perchlorate against thorin. Total volume is measured with a gas meter.

(d) Central Electricity Research Laboratory (C.E.R.L.) Method (See Ref. 42)

In this method, gas is drawn from the stack at 1 litre per minute and passed through a tube packed with glass beads. At the same time the glass beads are washed with 80% isopropyl alcohol to form a simple concurrent packed scrubber where most of the sulphur trioxide and sulphuric acid mist are dissolved. The remaining gas and the iso-propyl alcohol are then passed through an irrigated sintered glass disc where any mist is collected. From there the gas passes on and the iso-propyl alcohol with the so_3 dissolved in it is collected in a collecting flask. Analysis of sulphate is performed by precipitation of barium sulphate and measuring the turbidity of the resultant mixture. Alternatively, the sulphate can be analysed by Barium Perchlorate titration against thorin. Volume measurement is by way of flow meter and time measurement.

Comments

For the sampling of sulphuric acid mist, the method suffers because it is not isokinetic. Also, any sulphur dioxide dissolved in the isopropanol would have to be allowed for.

(e) British Standard Method (See Ref. 43)

The British standard method is based on the C.E.R.L. method except that analysis must be performed by Barium Perchlorate titration.

(f) N.S.W. Regulation Method (See Ref. 16)

The New South Wales method is based on the British standard method except that the sulphur dioxide absorbed by the isopropyl alcohol is extracted by bubbling nitrogen through the solution. There is also a difference in the method of analysis which is by gravimetric analysis of the precipitated Barium Sulphate.

Comments

A suitable method for general use but for the sampling of sulphuric acid mist, the method suffers because it is not isokinetic.

3.2.2 Automatic Methods

At the present time there are no instrumental methods for the determination of emissions of sulphur trioxide, mainly because below temperatures of 80-100°C, SO_3 exists as Sulphuric Acid mist.

4. SULPHUR DIOXIDE

Sulphur dioxide for many years was used as the yardstick of gaseous pollutants in the ambient atmosphere and this possibly explains the vast range of continuous recording analysers available to measure it.

Sources:-

Sulphur Dioxide in the atmosphere comes from a number of sources, both natural and man made. Natural sources are mainly related to volcanic action such as volcanos and fumaroles. The combustion of fossil fuels is the largest man-made source, while the smelting of sulphide ores, the refining of petroleum, the manufacture of sulphuric acid and the burning of refuse are also contributors.

Because of its adverse effects on property and vegetation and also its effects on health in the presence of suspended matter it continues to receive considerable attention in many industrialised countries. Australia is no exception although fortunately the situation is relieved by local sources of low sulphur bearing fuel.

Ambient concentrations of sulphur dioxide usually encountered in atmospheric pollution monitoring range between 10 to 3000 ug/m^3.

The numerous methods available for continuous monitoring of sulphur dioxide include conductometric, colourimetric, coulometric, flame photometric and more recently second derivative spectroscopy and pulsed fluorescence.

4.1 Ambient Levels

4.1.1 Manual Methods

(a) British Standard Method (See Ref. 44)

This method is a relatively cheap means of determining atmospheric concentrations of sulphur dioxide. Results obtained may be related to the World Health Organisation's Long Term Goals for sulphur dioxide. The method is applicable to a sampling period of 24 hours.

Ambient air is scrubbed through an acidified solution of hydrogen perioxide contained within a 250 ml dreschel bottle. Using standard alkali the nett acidity resulting from the reaction is determined by titration back to the original pH of the reagent, 4.5. The reaction equation is -

$$SO_2 + H_2O_2 - 2H^+ \ SO_4^=$$

A pH of 4.5 is used to prevent interference from carbon dioxide in the atmosphere. Interference from other acid and alkali gases present in the atmosphere does not make this method specific for sulphur dioxide. Under normal circumstances however sulphur dioxide is the predominant species measured - in excess of 70% of the total concentration measured.

Comments

This method is useful because it requires little expensive equipment and the values obtained relate to W.H.O. goals. However the method is not an accurate measure of sulphur dioxide in the air.

(b) Colourimetric - Pararosanoline (See Ref. 45 and 46)

Air is scrubbed through a solution of potassium tetrachloromercurate (TCM) in a bubbler, and a complex is formed. When this is reacted with pararasanoline and formaldehyde a purple dye is formed. The absorbance of this dye is proportional to the amount of sulphur dioxide dissolved. For further details see 4.12(b).

Comments

The method is more specific than the British Standard method but there are problems with the stability of the dyestuffs.

4.1.2 Automatic Methods

(a) Conductometric (See Ref. 47 and 48)

Historically, conductometric measurement was the principle first applied to the continuous measurement of sulphur dioxide. Sulphur dioxide is oxidised by hydrogen perioxide to form sulphate ions and in so doing increases the conductivity of the reagent solution. The reaction can be expressed -

$$SO_2 + H2O_2 - 2H^+ SO_4^{2-}$$

Early analysers adopting this principle had two conductivity cells - the first to determine the conductivity of the unreacted acidified hydrogen perioxide reagent and the second to likewise measure the conductivity of the reagent following its reaction with any sulphur dioxide present in the ambient air sample. The difference in conductivity is related to the concentration of sulphur dioxide present in the ambient air.

This type of analysis however is not specific to sulphur dioxide alone. Gases which form electrolytes in aqueous solution, or in other words increase the conductivity of a solution, interfere in such conductivity type measurements. Gases such as hydrogen chloride, nitrogen dioxide, hydrogen sulphide, chlorine and ammonia are some the gases which interfere. It is therefore more correct to apply the term 'acid gases' to the species measured using this technique. Interference from dissolved carbon dioxide at concentrations normally experienced in the atmosphere is eliminated by maintaining the peroxide reagent at a pH of 4.5.

Early commercial instruments had a lower measuring range of only 0-5500 ug/m and lacked the sensitivity to adequately measure general background levels in Sydney. Later commercial analysers became more portable, were less temperature dependent and provided a more useful lower range in the order of 5 to 1200 ug/m^3.

Comments

The main problem with these instruments is their poor selectivity for sulphur dioxide.

(b) Colourimetric (See Ref. 48)

Analysers are commercially available to measure sulphur dioxide based on the well known colourimetric West-Gaeke reaction.

If an air sample containing sulphur dioxide is scrubbed through a solution of potassium tetrochloromercurate (TCM), an extremely stable oxidant resistant complex is formed. This complex is then reacted with pararosanaline and formaldehyde to yield an intensely coloured purple dye pararosanoline methyl sulphonic acid. The absorbance of the resulting colour is measured spectrophotometrically in a liquid flow cell and is logarithmically proportional to the concentration of sulphur dioxide present in the air sample.

Due to the complex nature of the chemical reactions, the response time in continuous analysers is approximately 30 minutes. This technique is also suitable for batch type measurements up to 24 hours. Typical concentration ranges measured are between 25 to 1000 ug/m^3 although variations may be achieved by optimising certain sampling criteria, for example, flow rate.

Nitrogen dioxide, ozone and chlorine interfere with the reaction although the use of sulphonic acid in the reagent solution reduces the interference by chlorine. A prefilter will remove any interference by ozone.

Comments

This method suffers in that it relies on a complicated wet chemical technique and its associated problems.

(c) Coulometric (See Ref. 48)

Coulometric measurements of sulphur dioxide are based on the reducing properties of sulphur dioxide with a halogen contained within an electro-chemical titration cell.

A continuous air sample containing sulphur dioxide is scrubbed through a thermostatically controlled titration cell containing an aqueous solution of halogen, halide and sulphuric acid. In the presence of sulphur dioxide some of the halogen is reduced to halide. This reduction of halide concentration reduces the redox potential between the two electrodes in the titration cell. This potential is compared to a reference voltage and the current required to obtain the original redox potential is directly proportional to the concentration of sulphur dioxide in the air stream. The electrode reaction equations resulting when the halogen is bromine are

Cathode $SO_2 + Br_2 - SO_4^{2-} + 2\ Br^-$

Anode $2\ Br^- - Br_2 + 2e$

Commercial instruments available using this method normally have a measuring range of between 0-1500 ug/m^3 or 0 to 3000 ug/m3. Gases such as nitrogen dioxide, hydrogen sulphide, chlorine, ozone and mecaptans interfere with this analysis technique. The use of a chemical pre-filter will lessen the effect of such interferents although such multi-purpose filters are subject to a loss in efficiency, particularly over extended periods of use.

Reagent replenishment is not necessary in this type of instrument as it regenerates automatically. At least one commercial analyser has a useful inbuilt source of sulphur dioxide which enable automatic calibration.

Comments

This method though relying on a wet chemical principle is still popular.

(D) Solid Electrolyte Membrane - Faristor (See Ref. 48)

Another method for sulphur dioxide measurement is based on an amperometric reaction using a solid electrolyte membrane. The electrolyte is a gel-like organic compound which acts as a membrane between the two electrodes. Air is sampled through the electrolyte in the centre of the membrane, in contact with an inner electrode and the sulphur dioxide in the sample permeates through the membrane to the outer electrode, taking part in the electrochemical reaction. The membrane is claimed to be specific for sulphur dioxide but usually chemical prefilters are required to remove interfering gases. The range of the instrument is linear between 0.005 and 5 ppm. The gel electrolyte needs replacing several times a year. The stability of the method is doubtful and daily calibration is recommended. Temperature fluctuations cause changes in permeability of the membrane and some instruments have inbuilt temperature compensation.

Comments

The main disadvantage with this method are interferences from other gases, and the recharging of the gel. Their compact size is an advantage.

Comments

This method gives a sensitive and selective measure of sulphur dioxide in the atmosphere. However, the interference of other sulphur compounds requires a prefilter or chromatographic column. The technique also requires compressed hydrogen from a cylinder or preferably a hydrogen generator.

(g) Second Derivative Spectroscopy (See Ref. 48, 51, and 52)

The property of sulphur dioxide to absorb ultraviolet radiation is the principle which second derivative spectroscopy uses to determine ambient levels of sulphur dioxide. A technique which provides specific identification and quantitative analysis of the sulphur dioxide absorption peak makes this method superior to other recognised absorption techniques.

Ambient air containing sulphur dioxide is continuously introduced into a sample cell through which is focussed a narrow band ultraviolet source. Any sulphur dioxide present will strongly absorb this ultraviolet radiation and a light sensitive photomultiplier tube detects the resulting absorption which is characteristic to sulphur dioxide.

A mechanical wobbler is utilised in order to oscillate the wavelength around the absorption peak and in so doing a precise measurement of curvature or rate of change of the absorption peak is achieved. Although other gases may absorb around or at the particular sulphur dioxide absorption band, their influence is removed since other gases do not have an identical absorption curvature as sulphur dioxide, at the wavelength measured.

The analysis is insensitive to problems commonly experienced with analysers using absorption techniques such as lamp-ageing and water vapour. Gas flow rate does not effect the readout rate. Gas flow rate does not effect the readout rate. The analyser incorporates an automatic internal calibration source and two ranges, 0 to 1500 ug/m^3 and 0 to 6000 ug/m^3, are available.

This technique provides flexibility since other gases such as nitric oxide and ammonia may be analysed simply be changing wavelengths.

Comments: This technique offers a principle without consumables, with good selectivity for sulphur dioxide and is not dependent on sample flow. The source lamp however requires replacement every three months.

(h) Remote U.V. Detection (See Ref. 48 and 53)

One of the more recent developments for the measurement of sulphur dioxide is a remote sensing correlation spectrometer which measures the concentration of the pollutants between the sensing device and a U.V.-Visible source. The U.V.-Visible source is either solar radiation for vertical pollution monitoring or an artificial quartz-iodine or high pressure Zenon arc lamp for ambient air monitoring. For air monitoring the advantages of the system are that it is specific for sulphur dioxide, it gives an average value over the distance of sampling (up to 1,000 metres), it prevents loss in sample lines and is almost instantaneous in readout.

The sensing instrument contains two telescopes to collect light from the source, a dual grating spectrometer for dispersion of the incoming light, a disc-shaped exit mask or correlator and an electronics system. The correlator functions as a high-contrast reference spectrum for matching against the incoming spectra and is composed of arrays of circular slits photoetched in aluminium on quartz. The slits are designed to correlate sequentially in a positive and negative sense with absorption bands of sulphur dioxide, by rotation of the disc in the exit plane. Energy modulation is determined by a photomultiplier and transmitted as an electronic voltage which is linearly proportional to the gas concentration in the range 3 to 2000 ug/m^3 when measured over a 1,000 meter range.

Comments. The unique feature of this technique is that it measures the average sulphur dioxide concentration over a distance and not from a point source as do other monitors. It is a very expensive instrument.

4.2 Source Levels

There are a large number of methods for the testing of sulphur dioxide in emissions from stationary sources, both manual and instrumental Manual methods have traditionally been used for many years but with improved technology now available at reasonable cost, instrumental methods are preferred.

4.2.1 Manual Methods

Most manual methods for the measurement of sulphur dioxide emissions are made simultaneously with the measurement of sulphur trioxide and are performed with the same sampling train. That is, having removed the sulphur trioxide from the sampled gas stream, sulphur dioxide is then absorbed and analysed.

(a) Intersociety Committee on Methods of Air Sampling and Analysis Method (See Ref. 39 and 40)

Following sulphur trioxide removal by controlled condensation, the sulphur dioxide containing gas is then passed to a bubbler containing 3% hydrogen peroxide solution. The sulphur dioxide is collected and oxidized to sulphuric acid. The sulphate is then analysed by a colourimetric procedure using Barium Chloronilate or by titration with either sodium hydroxide or barium perchlorate. Flow rate should be limited to 1 litre/min.

(b) U.S. E.P.A. Method 6 (See Ref. 4, 17, and 18)

Sulphur trioxide is removed by scrubbing with 80% isopropyl alcohol and the gas passed to 2 midget impingers containing 3% hydrogen peroxide in an ice bath. The sulphur dioxide is collected and oxidized to sulphur acid and analysed by titration using Barium Perchlorate against Thorin.

(c) U.S. E.P.A. Method 8 See Ref. 4,17,18 and 19)

This is specifically for the determination of sulphur oxides emission from Sulphur Acid Plants. After the removal of Sulphur Trioxide/Sulphur Acid Mist, the gas is passed to 2 Greenburg-Smith impingers in an ice bath at the flow rate of 30 litres/minute, where the sulphur dioxide is collected and oxidized to sulphuric acid. This is analysed by Barium Perchlorate/Thorin titration.

(d), Central Electricity Research Laboratory
C.E.R.L. Method (See Ref. 42)

After the removal of sulphur trioxide from the stream, the gas is passed to a bubbler containing a measured quantity of an iodine solution. The iodine is decolourized by the sulphur dioxide and the time taken for this decolourization (at a flow of 1 l/min) is proportional to the sulphur dioxide concentration.

Comments. The method is not specific for sulphur dioxide and other oxidising or reducing gases interfere. Volatilization of iodine and absorption of sulphur dioxide in isopropyl alcohol introduces errors.

(e) British Standard Method (See Ref. 43)

The British standard method is identical to the C.E.R.L. method except that the small quantity of sulphur dioxide absorbed by the isopropyl alcohol is also estimated.

Comments. As for (d) above except that the sulphur dioxide in the isopropyl alcohol is allowed for.

(f) N.S.W. Regulation Method (See Ref. 16)

Similar to the British Standard Method except that instead of decolourizing the iodine solution, the test is stopped before total decolourization. Instead of following the iodine bubbler with an empty moisture trap, it is followed by a bubbler containing an equivalent amount of sodium thiosulphate. This measure ensures that iodine volatilized from the solution is collected by the thiosulphate and is not calculated as sulphur dioxide. After sampling the contents of the two bubblers are mixed and the sulphur dioxide concentration calculated by back titration with iodine.

Comments. Overcomes most of the problems of (d) & (e) above but is still subject to interferences in some situations.

(g) Gas Detector Tubes (See Ref. 54. 55 and 56)

A known volume of air or stack gas at a standard flow rate is drawn through a glass tube containing a solid adsorbant impregnated with a reagent that reacts with sulphur dioxide to form a coloured stain. The length of the stain or depth of the colour is proportional to the quantity of sulphur dioxide in the air being tested.

Usually the air is sampled by means of a portable hand pump which is factory calibrated or can be calibrated as shown in reference 54 and 56. The pump delivers a known amount of air at a standard flow rate.

Pumps and tubes are commercially available from a number of manufacturers or can be made in the laboratory. This method is applicable to measurements of many other gaseous pollutants, both ambient and stack levels. The reagent, which is sensitive to the specific pollutant being measured, is the only difference in the methods.

Comments. These tubes should only be used as an indicator only and not for accurate analysis.

(h) Canadian E.P.S. Method (See Ref. 57)

Very similar to the U.S. E.P.A. Method 6.

4.2.2 Instrumental Methods

Instrumental methods can be divided into three classes, those that withdraw a representative sample, condition it and measure the sulphur dioxide concentration, those which measure in-situ in the duct, and those which could be described as remote sensing.

(a) Non Dispersive Infra Red

This was the first of the continuous methods of measurement of sulphur dioxide to become accepted. Gas is drawn from the stack through a heated particulate filter, through a heated (100°C) line to a refrigeration unit to remove water vapour, and then to the instrument. The accuracy of detection in NDIR instruments is not dependent on sample flow rate.

The principle is that IR energy is absorbed quantitatively by Sulphur Dioxide. The narrow band IR source is chopped into two identical beams, which are alternatively transmitted through a sample gas cell and a reference gas cell before passing into a detector cell. The detector contains a gas which absorbs energy at a particular wavelength thus heating and expanding the gas. When sulphur dioxide is not in the sample flow cell, equal energy reaches the detector which remains in balance.

When sulphur dioxide passes through the sample cell, absorption of the IR energy occurs and the detector becomes imbalanced, alternatively heating and cooling the gas sealed in the detector cell. By using a metallic diaphragm as part of a capacitor the pulsing of the capacitor plate is converted into a D.C. voltage.

Interferences caused by co-existing gases such as carbon dioxide, nitrogen oxides and water vapour can be reduced by including concentrations of these gases in the reference cell. Water vapour is largely removed by the refrigeration step.

A refinement of this type of instrument involves the alternative measurement of the degree of absorption in the sample at two selected wavelengths. One of these wavelengths corresponds to an absorption peak in the measured component, and the other is a nearby wavelength where the absorption is low. The absorption at the latter wavelength is used as a reference to compensate for changes in energy caused by dirty cell windows, change of detector sensitivity and water vapour, so that no refrigeration is necessary.

The instrument is calibrated with gas calibration standards or with permeation tubes, which can be inbuilt for automatic calibration.

Comments. This is a well proven method and the only problems that arise in use is usually with the sample conditioning.

(b) Faristor - Solid Electrolyte Membrane

This instrument operates on the same principle as the ambient instruments (4.1.2 d). Sample conditioning is necessary and this would involve particulate removal, withdrawal of sample through a heated line, refrigeration to remove water vapour, and for this type of instrument, removal by prefilters of interfering gases such as nitrogen. oxides.

Comments. Interferences of other gases is a source of concern. as is sample conditioning.

(c) U.V. Pulsed Fluorescence Method

This method also involves the withdrawal of a sample from the stack through a filter, a heated line and a refrigerator. It operates on the same principle as the ambient instrument (4.1.2 e).

Comments. The principle gives sensitive interference free measurement and the problems would be only with sample conditioning.

(d) Flame Photometry Method

The sample is drawn from the stack, through a filter and heated line. The analyser unit is the same unit as the ambient monitor (4.1.2.f), so the gas must be diluted with clean air before going to the separation column. This step removes the necessity to remove water vapour. As with the ambient analyser, a simultaneous analysis of methyl mercaptan and hydrogen sulphide can also be obtained.

Comments. It has the ability to also measure other sulphur compounds but it needs compressed hydrogen as a consumable.

(e) Second Derivative Spectrometer Method

This is a method involving the simultaneous determination of sulphur dioxide and nitric oxide insitu. The principle of measurement is the same as the ambient monitor, (4.1.2 g), that of derivative spectroscopy. but the operation of the instrument is different. The sample cell is at the end of a probe with the spectrometer and electronics at the other end. The probe is inserted into the stack with the spectrometer outside. The sample cell is sealed with an alundum thimble so that stack gas will diffuse through the cell. but particulate matter will be excluded. The light path is from the spectrometer, through the probe. through a quartz window into the sample cell where it is reflected back to the spectrometer by a reflector in the end of the sample cell. The instrument has inbuilt calibration using sealed cells of the measured gas and inbuilt zero.

Comments. The sensor sited inside the gas stream being measured, is a significant plus factor.

(f) Remote U.V. Detection

This method uses the same apparatus as the ambient monitor (4.1.2 h). Its value in source monitoring lies in its ability to measure levels of sulphur dioxide in a plume from a distance. It would be set up to scan a number of stacks or to follow the path of a plume.

However, it is not a method for continuous measurement or measurement for regulation purposes.

Comments. Its advantages lie in the ability to sense remotely. Its disadvantages are its cost, its poor accuracy and it is not really meant for continuous use.

5. CARBON MONOXIDE

Carbon monoxide can occur as a pollutant in the atmosphere in concentrations greater than any other gaseous contaminant. Concentrations vary from approximately 1 to 120 mg/m^3. The motor vehicle if the major source of carbon monoxide and in large cities contributes to most of the ground level concentrations measured. Carbon monoxide is formed as a result of incomplete combustion of fossil fuels.

5.1 Ambient Levels

5.1.1 Manual Methods

(a) Gas Detector Tube (See Ref. 58)

The principal is described in 4.2.1 (g). The tubes are frequently used for the estimation of carbon monoxide in ambient concentrations.

Comments

The tubes should only be used as an indication of the levels encountered and not for accurate measurement.

5.1.2 Automatic Methods

(a) Non-dispersive infra-red (NDIR) (See Ref. 59)

The ability of carbon monoxide to quantitatively absorb infra-red radiation is the property which most ideally lends itself to instrumental analysis of carbon monoxide.

The principle of NDIR is described under section 4.2.2 (a) for sulphur dioxide.

The major interference to this method for the determination of carbon monoxide is water vapour. Without correction the error could be as high as 12 mg/m^3. This interference however can be effectively minimised by passing the air sample through a drying agent such as silica gel or by passing it through a dehumidifier or simply by saturating the air sample prior to analysis. Other more minor interferences are carbon dioxide and some hydrocarbons and these can be reduced by adding typical atmospheric concentrations of these gases to the reference call.

The path length of the sample cell determines the sensitivity of the instrument and with a path length of a metre, a measuring range of 120 mg/m^3 is usual.

Recent instruments however claim an increase in sensitivity of about 10 fold.

Comments

This is the accepted method for the long term measurement of carbon monoxide. Water vapour is the only real interference and hence the need to stabilise the water vapour content of calibration and sample. The fixed cell length means the sample flow rate is not critical and there are no consumables.

(b) Hopcalite or Specialised Catalytic Combustion Analysers (See Ref. 60)

Catalytic combustion analysers rely on a heated catalytic filament, which is part of a wheatstone bridge circuit and is increased in temperature by combusting sample gases in the presence of oxygen. This increase in temperature causes an increase in resistance of this arm of the circuit, which is proportional to the concentration of carbon monoxide passing over the catalytic filament. This principle should not generally be applied to the detection of carbon monoxide because of the interference from other gases.

However there are detectors available with a low temperature catalyst called "Hopcalite", which is highly selective for carbon monoxide, the temperature stabilised detection cartridge is composed of Hopcalite and any carbon monoxide in the sample air, when passing through this cartridge, is catalytically oxidised to carbon dioxide with the liberation of heat. A thermister in the Hopcalite gives an increase in voltage proportional to the concentration of carbon monoxide. Water vapour is a poison for Hopcalite and the sample air must be predried. The detection range of this method is limited to 10-600 mg/m^3 and this is not very suitable for ambient air monitoring.

Comments

The method is not very sensitive and is not suitable for most atmospheric applications.

(c) Electrochemical

A recent development for the detection of carbon monoxide in ambient levels is by an electrochemical principle using a catalytically active electroce in the detector cell. Carbon monoxide is oxidised to carbon dioxide in an aqueous sulphuric acid electrolyte at a platinum electrode as in the following equation -

$$CO + H_2O = CO_2 + 2H^+ + 2e$$

Air is sampled in the instrument and after humidification it diffuses through an electrochemical sensor. The sensor contains a sensing electrode (anode), a reference electrode, a counter electrode and concentrated sulphuric acid as the electrolyte. The electrooxidation of carbon monoxide occurs at the sensing electrode while the counter electrode acts as the cathode, and the current flows between the sensing and the counter electrode. The current generated by this electrochemical oxidation of carbon monoxide concentration in the air sample in the range 0-120 mg/m^3, 0-600 ug/m^3.

Comments

Several gases interfere with the reaction including nitric oxide, acetylene and ethylene but at ambient levels nitric oxide is the only serious interference. A prefilter is available to remove nitric oxide. The instrument is very portable and ideal for short term use. For continuous monitoring the reaction cell is replaced every 4-6 months.

5.2 Source Levels

5.2.1 Manual Methods

(a) Absorption Method (See Ref. 61)

There are a number of gas analysis apparatus available for absorption methods. These include Orsat's (the most popular) and Hempel's and Bunte's apparatus. The principle used is the absorption of carbon monoxide by ammoniacal cuprous chloride. Gas is drawn from the stack into the absorption apparatus by the use of a levelling bottle and carbon dioxide and oxygen are first absorbed. The carbon monoxide is then absorbed by the reajent and the decrease in volume is measured.

Comments

This is a very simple technique using inexpensive equipment. However, the accuracy is poor because errors from the absorption of carbon dioxide and oyygen are additive to the errors for the carbon monoxide determination.

(b) Combustion Method (See Ref. 62)

Carbon Dioxide is first removed (and measured) by a method similar to the absorption method. The gas is then passed over a copper oxide catalyst at 275°C where the carbon monoxide is oxidized to carbon dioxide which is then measured as in the absorption method.

(c) Gas Detector Tube

The method is described in 4.2.1(g)

Comments

The method is not very satisfactory for source use, because of measuring errors and the lack of sample conditioning.

5.2.2 Automatic Methods

(a) NDIR.

The method is described under 5.1.2 (a) and 4.2.2 (a).

Comments

As for 5.1.2 (a) In source concentrations water vapour causes less interferences to the measurement of carbon monoxide.

(b) Catalytic Combustion

This principle is described in Section 5.1.2 (b) and for source concentrations usually employs the catalytic filament.

Comments

In source use these instruments tend to be unsatisfactoy as they respond to other combustible gases and are not specific for carbon monoxide.

6. NITROGEN OXIDES

Nitrogen oxides in this paper refers to nitric oxide and nitrogen dioxide.

Sources:-

Nitric oxide is a by product of fossil fuel combustion and occurs from the oxidation of nitrogenous compounds in the fuel but mainly from oxidation of the nitrogen in the combustion air. Generally the higher the temperature of combustion the more nitric oxide produced.

The largest sources are motor vehicles, fossil fuel power generation and fossil fuel boilers. Minor sources are nitric acid plants, other chemical operations using nitric acid and any other process using fossil fuels as a heat source.

In fuel burning more than 90% of the oxides of nitrogen formed is nitric oxide. Nitric oxide slowly oxidises in the air to nitrogen dioxide. The main concern about ambient concentrations of nitrogen oxides is because they are "precursers" to photochemical smog or ozone.

Both oxides will be discussed together and the methods will be noted as applying to one or both oxides.

6.1 Ambient Levels

6.1.1 Manual Methods

(a) Colourimetric (Nitrogen Dioxide and Nitric Oxide)

(See Ref. 63 & 64)

The principle is described later in 6.1.2(a).

Comments

The method is suitable for short term samples of nitrogen dioxide but unsuitable for measurement of nitric oxide.

(b) Jacobs - Hochheiser Colourimetric (Nitrogen Dioxide) (See Ref. 65)

Nitrogen dioxide may be determined colourimetrically using the Jacobs - Hochheiser method. It is similar to the Saltzmann technique although it is not applicable to continuous automatic measurement.

Ambient air containing nitrogen dioxide is bubbled through a teflon, polypropylene or glass bubbler containing a solution of sodium hydroxide at a flow rate of 0.2 litres per minute. The formation of a very stable solution of sodium nitrite resultes.

Following sample collection, the resulting nitrite ion is reacted with phosphoric acid, sulphanilamide and N-1 naphthylethylenediamine dihydrochloride which forms a red azo-dye. The colour produced is measured spectrophotometrically. Interference by sulphur dioxide is eliminated by adding hydrogen perioxide prior to analysis.

Comments

This method is satisfactory for the collection of batch samples of up to 24 hours duration within a concentration range of 20 to 740 mg/m^3.

(c) Gas Detector Tubes (Nitric Oxide and Nitrogen Dioxide)

The principle is described in 4.2.1 (g)

Comments

The tubes should be used as indicators only and not for accurate analysis.

6.1.2 Automatic Methods

(a) Colourimetric (Nitrogen Dioxide and Nitric Oxide)

(See Ref. 63 and 64)

The long established Slatzmann method can be used to colourimetrically determine ambient concentrations of nitrogen dioxide on an automated basis.

A known volume of air is continually passed through a bubbler containing an acetic acid solution of N-1-napthlethylenediamine dihydrochloride. The nitrite ion formed in the reaction froms a red azo dye the intensity of which is then measured using a photocell. The optical absorption due to the red dye is then compared to the light absorption of the unreacted reagent through the reference flow cell. The optical absorption is logarithmically proportional to the concentration of nitrogen dioxide in the air sample

This technique is specific to nitrogen dioxide. However the response time is slow, corresponding to the time required for the red dye to form. Liquid and air pumps, flowmeters, large quantities of glassware and plumbing makes this method troublesome and difficult to keep running.

The method is used to measure nitric oxide by pretreating the air with an oxidising medium such as hydrogen perioxide, acidified potassium permanganate or chromic acid the resulting nitrogen dioxide may be analysed as outlined above. It is not recommended however as the oxidation is usually only about 70-80% efficient.

Comments

The method is not recommended for continuous measurement of nitrogen oxides.

(b) Coulometry (NO and NO_2)

The principle of coulometry as applied to the measurement of nitrogen dioxide is similar to that for sulphur dioxide measurement as previously discussed in Section 4.1.2 (c).

In this measurement however, the electrolyte consists of an aqueous solution of potassium iodide which is within a thermostatically controlled cell containing two electrodes. The iodide ions in solution react with nitrogen dioxide to form the tri-iodide ion which is then reduced at the cathode to form iodine. The electrode reaction at the cathode produces an electric current which is measured, amplified and recorded on a strip chart recorder. This measurement is directly related to the concentration of nitrogen dioxide in the ambient air sample.

Facilities for automatic zero and span calibrations are available in commercially available instruments.

Interferences such as hydrogen sulphide, hydrogen chloride, ammonia and chlorine are claimed to be effectively removed by the use of a chemical filter prior to the reaction cell. However, there is doubt regarding the efficiency of such filters as previously discussed in Section 4.2.1.

Nitric oxide may be measured using this technique by first passing the ambient air sample through a suitable oxidation medium. The nitrogen dioxide resulting from the oxidation is them measured using the identical procedure as discussed above.

Comments

Recent automatic methods, particularly chemiluminesence, has made their method somewhat obsolete.

(c) Chemiluminescence (Nitric Oxide & Nitrogen Dioxide)

(See Ref. 66 and 68)

Nitric oxide can be measured using the principle of chemiluminescence. Nitric oxide (NO) reacts with ozone (O_3) to form oxygen and about 10% electronically excited nitrogen dioxide (NO_2). Transition of the excited nitrogen dioxide to its normal ground state does so with the emission of light of a certain wavelength according to the following reactions.

$$NO + O_3 - NO_2^* + O_2$$

$$NO_2^* - NO_2 + hv \quad (600\text{-}3{,}000nm)$$

The resulting light emission, which is measured by a light sensitive photomultiplier tube and amplified, is proportional to the amount of nitric oxide present in the ambient air sample.

As applied to instrumentation, a continuous stream of sample air is drawn into a reaction chamber where it is mixed with a stream of ozone-rich oxygen. The actual reaction takes place immediately prior to the photomultiplier cathode surface. In earlier instruments the reaction took place under vacuum however in latter analysers the reaction occurs near atmospheric pressure. Analysers of this type can be used to measure nitric oxide concentrations up to 1%, although for ambient applications, les than 200 mg/m^3, the photomultiplier tube should be thermo-electrically cooled to below - 10°C. Using this technique then offers a continuous linear output between 5 ug/m^3 to 1%.

Chemiluminescence also lends itself to the measurement of nitrogen dioxide. A catalytic converter is used as a means of converting any nitrogen dioxide present in the ambient air stream to nitric oxide. The resulting nitric oxide is then analysed by the technique as outlined above and so in most commercially available analysers both nitric oxide and nitrogen dioxide can be simultaneously determined. Converters normally used are of stainless steel, molybdenum or gold all of which operate at high temperatures. Charcoal may also be used, however, it has to be periodically replaced. On the credit side charcoal suffers less ammonia interference and is highly efficient in reducing nitrogen dioxide.

Comments

Chemiluminescence is the accepted method for nitrogen oxide measurements but for nitrogen dioxide measurement does suffer from interferences from some other nitrogen containing gases such as PAN and nitric acid.

(d) Solid Electrolyte Membrane. (NO and NO_2)

Analysers of this type use the same principle as that previously discussed for sulphur dioxide (Section 4.1.2 (d)). The only difference is that a membrane specific to nitric oxide or nitrogen dioxide is used.

Comments

As for 4.1.2 (d).

(e) Remote UV Detection (NO2) (See Ref. 53)

Again this technique is identical to that discussed for sulphur dioxide (Section 4.1.2 h) except that the wavelengths measured in the correlation spectrometer are those due to nitrogen dioxide. The range of detection is linear over the range of 3 to 2000 ug/m^3 over a measured distance of approximately 1000 metres.

A combined instrument which measures both sulphur dioxide and nitrogen dioxide is commercially available.

Comments

As for 4.1.2 h.

(f) Second Derivitive Spectroscopy (NO & NO2) (See Ref. 145)

Nitric Oxide like sulphur dioxide, characteristically absorbs energy in the ultraviolet region. The principle is also applicable to nitrogen dioxide, which absorbs energy in the visible region.

The principal is described in Section 4.1.2 (g).

Comments

As for section 4. (g).

6.2 Source Levels

As with sulphur dioxide there are a large number of methods for measuring nitric oxide emissions, both instrumental and manual. However most manual methods for nitric oxide measurement are in fact methods for nitrogen dioxide and involve, as a first step, the oxidation of nitric oxide. This oxidation step is critical and is subject to many errors, rendering these methods inaccurate. Instrumental methods are specific and accurate and manual methods for the estimation of nitric oxide from stationary sources are being phased out.

6.2.1 Manual Methods

(a) Colourimetric Methods (NO and NO_2) (See Ref. 16, 65 and 67)

The method of Saltzmann and the method of Jacobs - Hochheiser can be used for source testing. In this method, gas is drawn from the stack through a heated probe, a bubbler or oxidizing agent, a bubble of absorbing solution, a pump and a gas meter and the analysis performed as described in the ambient methods.

The main difficulties in this method arise from the fact that almost all nitrogen oxides emitted from stationary sources are as nitric oxide and so the oxidizing step is critical.

Comments

Because of the inefficiency of the oxidation step and the interference due to sulphur dioxide the method is somewhat outdated.

(b) Gas Detector Tubes (NO and NO_2)

The principle is described in 4.2.1 (g).

6.2.2 Instrumental Methods

(a) Non Dispersive Infra red (NO and NO_2)

The non-dispersive Infra red technique can be used to measure nitrogen oxides, using a different analyzer for nitric oxide and nitrogen dioxide. The gas is drawn from the stack by a heated probe, heated line, heated particulate filter and refrigerated condensor to the instruments. The instruments are calibrated using standard gas mixtures (NO) or pemeation tubes (NO_2). The principle is described in 4.2.2 (a).

Comments

The method is reliable in operation but suffers from interferences. The preconditioning step tends to reduce the NO_2 in the gas stream.

(b) Second Derivative Spectrometry (NO)

This is a method involving the simultaneous determination of sulphur dioxide and nitric oxide. See 4.2.2 (e) for details.

(c) Chemiluminescence (NO and NO_2)

The instrument is similar to that used in ambient sampling. There are two alternative sampling methods. Gas is drawn from the stack through a heated line and a particulate filter to a dilution module where the gas is diluted approximately 3000 to 1. This diluted gas is then passed to an ambient monitor. Alternatively, a stack monitor able to read concentrations from 0 to 2000 ppm nitric oxide and nitrogen dioxide can be used. In this case, gas is drawn through a heated line, a particulate filter and a refrigerated condenser to the instrument. These instruments are calibrated using standard gas mixtures. For further details see 6.1.2 (c).

Comments

The method is very satisfactory, being sensitive and selective and using no consumables.

(d) Solid Electrolyte Membrane (NO and NO_2)

Using the same principle as already discussed (Section 4.2.2 (b)), nitric oxide and nitrogen dioxide can be measured. The gas is drawn from the stack though a heated line, a heated filter and a refrigerated condenser to the instrument. The instrument is calibrated using a standard gas mixture (NO) or permeation tubes (NO_2).

Comments

The instrument is compact but can suffer interferences from other gases.

(e) Remote Sensing UV (Nitrogen Dioxide)

This technique is as already discussed in section 4.1.2 (H) and 4.1.2 (f). It can only be used to measure nitrogen dioxide and is not particularly useful for source testing.

(f) Second Derivative Spectroscopy (NO and NO_2)

This technique uses the same instrument as discussed in Section 4.1.2 (g).

7. HYDROCARBONS

Naturally occurring hydrocarbons are present in the atmosphere as a result of transpiration and decomposition of vegetation and the escape of natural gas into the atmosphere and also volcanic action. Automobiles, combustion of fossil fuels at stationary sources and petroleum processing and handling are sources of hydrocarbons in industrialised cities.

Naturally occuring methane is present in the atmosphere at approximately 1 mg/m3 while total hydrocarbons range between 1 and 7 mg/m^3.

Methane is of little importance as a pollutant. However non-methane hydrocarbons are of prime importance as precursors in photochemical smog and, similarly, to nitrogen oxides, early morning hydrocarbon concentrations are a contributing factor to the potential ozone level later in the day.

The choice of technique in the measurement of hydrocarbons is simple. There is only one method and it is based on hydrogen flame ionisation detection.

7.1 Ambient Levels

7.1.1 Manual Methods

There are no manual methods used for the estimation of ambient concentrations of hydrocarbons.

7.1.2 Automatic Methods

(a) Hydrogen Flame Ionisation Detector (See Ref. 7, 69, 70, 71 and 72)

Continuous measurement of hydrocarbons using hydrogen flame ionisation detection relies on the measurement of ionised carbon atoms by burning the hydrocarbons in the sample in a hydrogen flame.

In commercially available instruments, hydrogen from a cylinder or hydrogen generator passes through a fine jet in the presence of a small flow of sample air. The hydrogen jet, incorporating an ignitor filament, acts as one electrode and an electrical potential is applied between this and a nearby collector electrode. The detector current is measured by means of a sensitive electrometer circuit. When organic gases burn in the flame, they emit electrons to produce a current which is directly proportional to the number of carbon atoms passing through the flame. The response for methane is linear in concentration ranges of 0.03 mg/m^3 to the percent range. The response is approximately linear for members of a homologous series of hydrocarbons and is used as an organic "carbon counter". Functional groups containing oxygen, halogens etc. tend to give relatively lower responses than expected and the detector has very low response for carbon dioxide, carbon monoxide, sulphur dioxide, water vapour etc.

Some current analysers available offer a dual sampling and detection system which facilitates a continuous output of both methane and non-methane hydrocarbon concentrations. One major difficulty concerning the determination of non-methane hydrocarbons is the efficiency of the stripper which separates them from methane. At present there are no manufacturers of hydrogen flame ionisation detectors who can claim a 100% efficient stripper.

For ambient determinations this instrument is the only practical means available. The instrument does suffer the disability of not being able to separate different hydrocarbons unless the sample is passed through a gas chromatographic column before the detector.

There are air quality chromatographs available which can separate the non-methane component into acetylene ethane ethylene and the remaining non-methane hydrocarbon content. Also by the catalytic conversion of carbon monoxide to methane, this pollutant can also be determined using this chromatographic technique.

The more specific methods relating to the detailed analysis of the different non-methane constituents are discussed in the following methods.

(b) C_2 - C_5 Hydrocarbons (See Ref. 73, 74 and 75)

Ambient hydrocarbons analysis give continuous measurements of methane and total hydrocarbons. The quantities and concentration of each individual hydrocarbon are a measure of their photochemical reactivity, source and age of the air parcel.

All methods in this type of analysis involve the use of gas chromatography. Samples are taken directly from the air, or from bags brought from other locations and either preconcentrated in liquid nitrogen or oxygen or injected directly onto the chromatograph.

Comments

The method offers very accurate detailed analysis but requires a significant scientific backup.

(c) High Molecular Weight Hydrocarbons (See Ref. 76)

High molecular weight hydrocarbons, although present in small concentrations are very important in air pollution studies because of their high reactivity in photochemical reactions in the atmosphere. The hydrocarbons are collected by absorption on organic porous polymers which do not absorb water. The sample is desorbed and separated by high-resolution (open tubular column) gas chromatography and identified by a mass spectrometry - computer technique.

Comments

As for (b) above.

(d) Mass Spectrometer - Freeze Out (See Ref. 77)

Hydrocarbons are collected in a freeze out trap by pumping air through a shepherd trap immersed in liquid nitrogen. The permanent gases are pumped off and water and carbon dioxide are reduced to an acceptable level by the use of absorbents. Following the removal of these compounds, the residual hydrocarbons are allowed to expand into a mass spectrometer and are analysed. This method does not measure methane.

Comments

As for (b) above.

(e) Infra Red Spectrometer (See Ref. 78)

Hydrocarbons in the atmosphere are collected in a modified shepherd trap immersed in liquid oxygen. Analysis is performed on an Infra red spectrometer calibrated against n-Hexane.

Comments

Methane is not collected and aromatics are not effectively measured.

7.2 Source Levels

7.2.1 Manual Methods

(a) Gas Detector Tubes

Some gas detector tubes are available for the estimation of hydrocarbons at source concentrations. The principle of gas detector tubes is described in 4.2.1 (g).

Comments

Gas detector tubes have a limited use only and should not be used for accurate estimation.

7.2.2 Automatic Methods

(a) NDIR

Using the non dispersive infra red principle, hydrocarbons can be measured from stationary sources. The particulates are first removed in a heated filter, the vent gas taken through a heated line, the water removed by refrigeration and the gas then passed to the analyser.

The principle is described in 4.2.2 (a) and relies on the absorption of infra red energy of a particular wavelength. Frequently the wavelength chosen gives almost linear measurement of parafins but only partial measurement of other hydrocarbons.

Comments

Except for the measurement of specific parafins this method is not suitable for analysis.

(b) Gas Chromatography

Gas Chromatography relies on the separation of the components in the sample on a column and then measurement of the individual components on a flame ionisation detector. See 7.1.2.

Comments

The method gives accurate measurement of individual hydrocarbons but in complex mixtures can be very tedious.

(c) Flame Ionisation Detector

Using a principle similar to the ambient instrument (see 7.1.2) this technique is the one normally used. The vent gas is filtered, pumped to the instrument via a heated line and passed to the flame. The instrument is calibrated using a known gas standard. It is a continuous analyser, only restricted by the supply of burner gas.

Comments

The instrument does not give equal response for some hydrocarbon compounds e.g. oxygenated or halides.

It also has less accuracy when the oxygen content of the sample is low, but this is usually overcome by using a nitrogen/hydrogen fuel. It is the usual method for hydrocarbon estimation.

8. FLUORIDES

Inorganic fluoride is present in the raw materials of many industrial processes and it is evolved in both gaseous and particulate form when these materials are heated to high temperatures or treated with acid. Manufacturers of aluminium, steel, glass, phosphate fertilizer, cement, bricks and ceramics are the main sources.

Fluorides act as cumulative plant poisons and gaseous fluoride at concentrations as low as 0.1 ug/m^3 can cause plant damage. Animals ingesting vegetation which has accumulated fluoride can be affected by fluorosis. This is especially prevalent among dairy cattle grazing near fluoride sources (see Ref. 79).

8.1 Ambient Levels

8.1.1 Manual Methods

(a) Dry Tube Method (see Ref. 80)

This is similar to the instument method using coated tubes (see 8.1.2) but the analysis is performed manually rather than instrumentally.

(b) Impinger Methods (see Ref. 81 and 82)

This method involves bubbling air through a solution of alkali. Particulate matter is usually removed by a membrane filter before the impingers and the two portions analysed separately. Gas volume is measured with a gas meter.

Comments

This method suffers from sensitivity problems and from problems associated with evaporation of the liquid in the impingers.

(c) Dry Filter Methods (see Ref. 83, 84, 85, 86 and 87)

Dry filter methods employ a filter impregnated with an alkali which collects the gaseous fluoride from the ambient air pumped through the filter. The particulate matter can be removed by a pre filter stage or the two fractions collected together. The filter is kept damp by adding glycerol to the impregnating solution.

Comments

These methods are generally efficient, sensitive and of low capital cost.

(d) Limed Papers (see Ref. 88)

In this method, papers impregnated with lime water are exposed to the atmosphere, under a rain cover, for periods of time, usually a month. The fluoride content is analysed and the results used as a relative measure of fluoride concentrations.

Comments

This method does not give a measure of the concentration in the atmosphere and is subject to meteorological influences which effect physical contact with the papers. These results are not comparable with other methods.

8.1.2 Automatic Methods (see Ref. 89)

These instruments are semi continuous in that they absorb fluoride from a batch of air and then analyse it automatically for its fluoride content.

One such instrument draws air through a spiral tube coated with an alkaline layer and the gaseous fluoride is absorbed on this layer.

The alkali containing the fluoride is then washed into a measuring cell, buffer added and the fluoride concentration automatically reed and recorded using a fluoride ion specific electrode.

Another instrument of similar principle uses a colourimetric procedure as end point analysis. This instruement also has slave units so that air can be drawn through coated tubes at a number of sites and only the tubes returned to the instrument for analysis.

Comments

Both these intruments suffer the disadvantage of being automated wet chemical procedures with the qualities of such instrumentation e.g. leaks, baseline drift, sensitivity problems, reagent problems etc.

8.2 Source Levels

8.2.1 Manual Method (see Ref. 16, 19 and 90)

Manual methods for the measurement of emissions of fluoride from stationary sources are based on isokinetic sampling of the gas stream and removal of the fluoride by filtration and absorption in an aqueous medium.

Air is drawn into the probes (heated if necessary) and the particulates removed in a paper thimble. To reduce gaseous fluoride absorption on the paper, they are impregnated with citric acid. The gaseous fluoride is then removed by impingers of sodium hydroxide.

Alternatively the two fraction can be collected together, sampling directly into impingers.

Analysis of stack emission samples should be performed by distillation (see Ref 84)

8.2.1 Automatic Methods -

These methods only measure gaseous emissions

(a) NDIR

Commercial NDIR monitors are not readily available but if due care is taken to selection of materials of construction this method is probably the most suitable for measurement of specific gaseous fluorides.

(b) Conductimetric Instruments

Similar in principle to the sulphur dioxide conductimetric monitor (see 4.1.1A) where a sample is dissolved in an aqueous medium and the increase in conductance of the solution measured and related to the fluoride concentration.

Comments

It is non specific - any soluble species in the gas stream will also register - and the method suffers from the usual disadvantages of automated "wet chemistry".

(c) Absorption - Ion Specific Electrode Method (see Ref. 91)

A vacuum pump draws flue gas and condensate through a flask containing sodium hydroxide solution. The air and liquid are separated, the air going to the pump and flow measuring device and the liquid to a cell where fluoride is measured with an Ion specific electrode.

9. HYDROGEN SULPHIDE

Hydrogen sulphide has a number of sources, both natural and man made. It is a gaseous product of the anaerobic degradation of biological matter and is emitted by volcanic action. In a similar fashion, it is a product of industrial processes where sulphur compoinds are processed under reducing conditions. Large emitters of hydrogen sulphide are petroleum refineries, Kraft Paper Mills, Carbon Black Manufacturers and most industrial processes using sulphur compounds

9.1 Ambient Levels

9.1.1 Manual Methods

(a) Colourimetric (see Ref. 19, 29, 92, 93, 94 and 95)

Air is drawn through a solution of p-aminodimethylaniline, ferric ion and chloride ion, in a bubbler, by means of a pump. The hydrogen sulphide reacts with the reagent to form methylene blue which is measured on a spectrophotometer at 670 nm. Alternativel the hydrogen sulphide is collected by bubbling through cadmium hydroxide and reacted to form methylene blue or Lauth's Violet.

Comments

It is a sensitive method for ambient use but sulphur dioxide interferes.

(b) Cadmium Sulphide Method

Air containing hydrogen sulphide is scrubbed through two bubblers in series containing ammoniacal cadmium chloride. Any hydrogen sulphide present will precipitate out as cadmium sulphide. The amount of cadmium sulphide precipitated is then estimated idometrically and may then be related back to the concentration of hydrogen sulphide in the air sample.

Comments - The method is sensitive for hydrogen sulphide measurements, up to approximately 700 ug/m^3.

9.1.2 Automatic Methods

(a) Colourimetric Method

A colourimetric technique for the automated analysis of ambient levels of hydrogen sulphide relies on the reaction of sulphide ion with a mixture of ferric chloride and p-aminodimethylaniline to yield methylene blue.

One commercially available analyser continually absorbs hydrogen sulphide in the ambient air through an alkaline suspension of cadmium hydro-oxide. An aliquot of the resulting sample is then passed from the absorption column to an analytical system where it is reacted with p-aminodimethylaniline and feric chloride to yield methylene blue. The intensity of the colour is then measured colourimetrically at 660 nm. Hydrogen sulphide is measured using this technique of over a measuring range of 3 to 300 ug/m^3.

Comment - This method is very specific for sulphide detection at low concentrations. Strongly reducing agents such as sulphur dioxide do interfere with colour development and a chromate filter may be used to remove this interference.

The "wet" chemistry involvement would make the method rather tedious.

(b) Flame Photometry

Hydrogen sulphide may be measured using the technique of flame photometry as discussed in Section 4.1.2. It may be measured in conjunction with sulphur dioxide and methyl mercaptan measurements or by itself.

Comments - This method is very satisfactory being very sensitive and selective but requires compressed hydrogen as a consumable.

(c) Paper Tape Sampler

The determination of ambient levels of hydrogen sulphide may be simply achieved by using a paper tape sampler identical to that discussed in Section 1.1.2 (a).

Filter paper sensitised with lead acetate is the reacting medium for the hydrogen sulphide present in the air sample. On contact with hydrogen sulphide the sensitised paper turns brown due to the formation of lead acetate. Samples collected in this manner are measured by comparing the light transmission through the stained filter to that transmitted through the blank filter. Using this transmission the concentration, in ug/m^3 hydrogen sulphide, present in the air sample may be determined by reading off a calibration curve.

This method requires that samples are read as soon as practicable following exposure, otherwise the brown lead sulphide stain will oxidise to form white lead sulphate on exposure to the atmosphere. To eliminate the interference of suspended matter on the filter paper a pre-filter is used. The method is sensitive for hydrogen sulphide measurements from 4 ug/m^3 to 30,000 ug/m^3.

9.2 Source Levels

9.2.1. Manual Methods

(a) Tutweiler Apparatus Method (see Ref. 96)

In this method, a gas sample is drawn into an impacted burette of Tutweiler design by raising and lowering a leveling bulb. The gas sample is reacted in small increments with standard iodine solution in the presence of starch indicator solution until all the hydrogen sulphide has been reacted.

Comments

Sulphur Dioxide and mercaptons interfere and have to be removed by prescrubbing.

(b) Ammoniacal Cadmium Chloride Method (see ref. 97)

In this method, a gas sample is drawn through a bubbler of Ammoniacal Cadmium Chloride. The precipitated Cadmium Sulphide is filtered off, washed, added to a closed wash bottle, and Hydrochloric acid and Iodine added. The liberated hydrogen sulphide reacts with the iodine and the excess iodine titrated with Sodium Thiosulphate. The gas is drawn through the bubblers with a simple train of probe, filter, bubblers, pump and gasmeter.

Comments

Sulphur Dioxide and mercaptons interfere and have to be removed by prescrubbing.

(c) Electrometric Titration Method (see Ref. 98)

In this method, a gas sample is drawn through a probe, filter and bubblers of Sodium Hydroxide which scrubs out hydrogen sulphide and mercaptorn, a pump and a gas meter. The Sodium Hydroxide solution is added to an ammoniacal alkaline solution and is titrated with aqueous silver solution, using as an indicator, the potential between a glass reference electrode and a silver sulphide indicating electrode. The end points for sulphide and mercaptons are indicated by separate inflections in the potential - volume curve.

(d) Colourimetric Procedures (see Ref 19, 29, 92, 93, 94 and 95)

These methods are an adaption of methods used in ambient measurement. Stark gas is aspirated through a solution of p-aminodimethylaniline, ferric ion and chloride ion, using a sample train of probe, filter, bubblers, pump and gas meeer. The hydrogen sulphide reacts with the bubbler contents to form methylene blue which is measured on a spectrophotometer at 670 nm.

Alternatively the hydrogen sulphide is collected by bubbling through Cadmium Hydroxide and reacted to form methylene blue or lauth's violet.

Comments

Sulphur dioxide interferes in this method.

(e) Dry Paper Tape Methods (see Ref. 16 and 99)

These methods are also an adaption of methods used in ambient measurement. Stark gas is drawn through a paper filter impregnated with a salt of an element which will give a dark stain of sulphide and the density of the stain is measured using a densitometer. The starck gas can be withdrawn by a sample train of probe, filter, pump and gas meter or by a calibrated hand pump. There are a number of compounds used to impregnate the tapes.

a) Silver nitrate

b) Argentocyanide

c) Mercuric Chloride

d) Lead Acetate

Comments

They all suffer from interference from Sulphur Dioxide (see Ref 99 and 100) and mercaptons and the gas stream must have a certain moisture content (not normally a problem with starck gas). Bleaching of the stain by exposure to light is also a problem. The most efficient impregnating salt is silver nitrate.

9.2.2 Automatic Methods

(a) Flame Photometric

This method is semi continuous (frequently sampling every 20 minutes), precise, sensitive and suffers no interferences. It is very quickly becoming the most reliable method of analysis for hydrogen sulphide.

The instrument is exactly the same instrument used for Sulphur Dioxide (see 4.2.2) in starck gas and can give a readout for Sulphur Dioxide, Hydrogen Sulphide, Methyl Mercaptan, Carbon Disulphide and Carbonyl Sulphide.

Comments

It is the only reliable method for the automatic measurement of hydrogen sulphide but uses compressed hydrogen as a consumable.

(b) Automated Paper Tape Method

The paper tape methods mentioned in manual methods (9.2.1e) can easily be automated. The tape is fitted into an instrument similar to the instrument used to measure suspended matter in the atmosphere (paper tape sampler, see 1.1.2). In this instrument the gas filters through the tape for a given time and a reading is obtained for an integrated sample over that time. The densitometer reading can be obtained either by removing the tape and reading manually or the instrument can be further automated by adding a densitometer.

Comments

The main disadvantages are interference by sulphur dioxide and light bleaching of the stain.

10 MERCAPTANS

The major sources of mercaptans are petroleum refining and draft pulp mill operations; minor sources are ferrous metallurgical operations. Mercaptans are of major interest in air pollution because of their extremely low odour threshold and their obnoxious odour.

10.1 Ambient levels

10.1.1 Manual Methods

Because of the extremely low concentration normally encountered in the atmosphere and the interference from the normally higher concentration of hydrogen sulphide and sulphur dioxide no manual method will be recommended.

10.1.2 Automatic Method

(a) Flame Photometry

The instrument described for hydrogen sulphide will measure mercaptans without interference.

10.2 Source Levels

10.2.1 Manual Methods

(a) Titration Methods (see Ref. 100 and 102)

These methods involve the collection of mercaptans in a solvent such as alcohol or by precipitation of sulphide. The quantity of mercaptan is determined by titration with Copper Alkyl Phtlalate or Iodine-Sodium Thiosulphate. A sample train of probe, bubbler/impinger, pump and gas meter is used for the collection.

Comments

Hydrogen sulphide interferes.

(b) Potentiometric Titration (see Ref 98, 103 and 104)

In these methods hydrogen sulphide and mercaptans are absorbed from the gas stream by bubbling through sodium hydroxide. The sampling train consists of probe, bubbler/impinger, pump and gas meter. The solution of mercaptans is added to an ammoniacal alkaline solution and titrated with aqueous silver nitrate. The end points for sulphide and mercaptans are indicated by separate inflections in the potential-volume curve.

(c) Colourimetric Methods (see Ref. 105 and 106)

Stack gas is drawn through a probe, bubbler or impinger, pump and gas meter. The mercaptans are collected by absorbing in a strongly acid solution of N, N-dimethyl p-phenylenediamine and ferric chloride. This produces a red complex which is measured at 500 nm on a Spectrophotometer.

Comments

Hydrogen sulphide interference can be minimized.

10.2.2 Automatic Methods

(a) Flame Photometry

The instruemnt described for hydrogen sulphide will measure mercaptans without interference.

11 OZONE

Ozone exists naturally in the upper atmosphere due to the action of ultraviolet radiation on oxygen. Ozone is formed near the earth's surface by the reaction of ultraviolet radiation on oxides of nitrogen and reactive hydrocarbons. Ozone, which forms over 90% of the oxidants in the atmosphere, can cause adverse effects on vegetation, rubber and health.

Ambient concentrations of ozone range between 0 and 1000ug/m3. The principle method for ozone measurement include colourimetry, coulometry, and chemiluminescence.

Ultraviolet radiation absorption is the most recent technique applied to the measurement of ozone.

Throughout the following discussion of the various methods employed for the measurement of ozone it will be seen that in some instances the term "oxidants" is used. Early generation instruments measured as wlll as ozone, peroxy acetyl nitrate (PAN), nitrogen dioxide and chlorine and this is expressed as "oxidants".

Of special note here in respect to the measurements of ozone is that a teflon filter and sampling line must be used. Although expensive, it is the only material available which does not significantly reduce the level of ozone as it passes through to the analyser prior to analysis.

11.1 Ambient Levels

11.1.1 Manual Methods

(a) Colourimetric (see Ref. 7, 107, 108, 109, 110, 111, 112, 113, 114, 115 and 116)

The traditional method of measuring oxidants was for many years, the sampling of air through a bubbler containing potassium iodide reagent (see 11.12a). The sample time was usually a period of 24 hours. The ozone oxidises the iodide to free iodine which can be measured photometrically as outlined in 11.1.2 or titrimetrically. Variations on this method use either neutral, alkaline, acidified or unfuffered iodide. Other methods use the colour produced by the reaction between ozone/oxidant and a dye which is measured by spectrophotometry.

Comments

The manual colourimetric analysis is unsatisfactory because sulphur dioxide negatively interferes and cannot be prescrubbed without removing ozone. The reagent is also unstable in daylight and has insufficient sensitivity and selectivity.

There are numerous other methods (see 117) but they find little use now that chemiluminesence has become available.

11.1.2 Automatic Methods

(a) Colourimetric (see Ref 119)

The ability of oxidants to react with an iodide solution to form iodine is the principle by which colourimetry may be applied to the measurement of oxidants. The reaction equation is $O_3 + 2KI + H_2O - O_2 + 2KOH + I_2$.

The iodine liberated in the reaction is then analysed colourimetrically. One instrumental method available, which is very similar in operation to the analyser used in the measurement of nitrogen dioxide, continuously draws an ambient air sample flowing through an absorption coil concurrent with the reagent solution. The solution, which colours following the liberation of iodine, passes on to a cell where the intensity is photometrically measured. The intensity of the colour is logarithmically related to the concentration of oxidant in the air sample.

Comments

This type of instrument suffers from the same disadvantages as those discussed for the colourimetric determination of nitrogen dioxide (see 6.1.2a). Reducing agents such as sulphur dioxide and hydrogen sulphide interfere in a negative sense to the actual concentration measured. A chromate scrubber can be used to oxidise the sulphur dioxide although, due to the instability of ozone, such a filter can dramatically reduce the level of ozone to be measured. Instruments of this type have ranges in the order of 0 to 4000ug/m^3.

(b) Coulometry (See Ref. 118)

An early principle applied to the continuous measurement of oxidents utilised the electrochemical oxidation-reduction reaction of potassium iodide by oxidants. The technique is similar to that used in the coulometric measurement of the oxidation of sulphur dioxide (Section 4.12 c) although here the ozone is reduced.

If an ambient air sample containing oxidants is passed through an electrochemical cell containing potassium iodide, oxidation of the iodide occurs at the cathode and free iodine is liberated. Due to a polarisation current, a very thin layer of hydrogen is also produced at the cathode. Reaction of the iodine with hydrogen occurs immediately which results in a repolarisation current due to the removal of the hydrogen.

The resulting current is then directly proportional to the concentration of oxidants in the air sample.

Instruments using this technique operate over a range of approximately 0 to 2000 ug/m^3.

Comments

Interference from sulphur dioxide may be eliminated by using a filter. However, as mentioned in the previous section, loss of ozone in the air sample will result.

(c) Chemiluminescence (See ref 66,117, 120 and 121)

The principle of chemiluminescence as applied in the measurement of nitric oxide may be similarly used for the continuous measurement of ozone. It is based on the gas-phase chemiluminescence reation of ozone, present in the ambient air sample, with ethylene gas, resulting in the emission of light in the visible region. The reaction takes place at the cathode surface of a light sensitive photomultiplier tube. The very small amount of light seen by the photomultiplier is converted to a current, amplified and finally displayed on a strip chart recorder. This reading is linearly related to the concentration of ozone in the air sample.

Comments

The Chemiluminescent measurement of ozone is a very sensitive technique and offers the following important advantages over other wet chemical methods.

(i) Specific for ozone

(ii) Very fast response time

(iii) Measurement ranges 0, - 500 ug/m^3 and higher

(iv) Minimum maintenance

(v) No wet chemicals required.

Compressed Ethylene however, is consumable. There are other materials available such as Rhodamine B which can be used to give a chemiluminescent reaction with ozone. Rhodamine B is more sensitive than ethylene although this sensitivity slowly degrades on reaction with ozone.

(d) Ultra Violet Absorption

The most recent principle applied in relation to the continuous measurement of ozone relies on the ability of ozone to absorb ultraviolet radiation.

One instrument currently available passes an air sample containing ozone through an absorption chamber which is continually exposed to a source of ultraviolet radiation. At one end of the chamber is a light sensitive photomultiplie tube which 'sees' the amount of ultraviolet light passing through the air sample following absorption by the ozone present. The air sample is alternately cycled, as a reference, through a catalytic convertor which converts any ozone present to oxygen. This air sample minus ozone is then passed through the absorption chamber and the amount of transmitted ultraviolet light is measured by the photomultiplier tube. The difference of ultraviolet light between the sample and reference measurements is then directly related to the concentration of the ozone in the sample. The measuring ranges available are from 0 - 1000 ug/m3 and higher. The advantages are similar to those listed under chemiluminescence and it is not flow dependant and it has no consumables. However, the presence of suspended matter in the sample may cause interference in the measurement and filteration may cause degredation of ozone.

11.2 Source Levels

Generally all the methods described for the ambient levels are applicable to the higher source levels.

12. CHLORINE

There are only a very few sources of chloride and these are related to manufacturers and users of the element. Major sources are chlor-alkali plants which manufacture both chlorine and caustic soda from brine, metallurgical plants which use chlorine gas or tablets of chlorine compounds as part of their process and pulp mills which use the gas as a bleaching agent. Minor sources are swimming pools, and users of the gas or its compounds to bleach or disinfect

12.1 Ambient Levels

12.1.1 Manual Methods

(a) O-Tolidine Method (See ref. 16, 107, 122 and 123)

Air is sampled through a bubbler and Chlorine is trapped in Sodium Hydroxide solution or directly in O-tolidine solution and a yellow colour produced by the reaction between chlorine and O-tolidine. The colour is read directly on a spectrophotometer at either 435 mm or 490 mm. Alternatively the colour is compared with colours produced by standard concentrations of Potassium Dichromate.

(b) Methyl Orange (See ref. 124 and 125)

Air is sampled through a bubbler containing a dilute solution of methyl orange. Near pH 3.0 the colour of methyl orange ceases to vary with acidity and the dye is quantitatively bleached by free chlorine and the extent of the bleaching can be determined colourimetrically.

Comments

Interference in the measurement is caused by Sulphur Dioxide, Nitrogen Dioxide, Bromine etc.

(c) Iodine - Thiosulphate (See ref. 19 and 107)

Air is drawn through a bubbler containing iodine. Chlorine in the air reacts to form the tri-iodine ion and the free iodine is titrated with thiosulphate.

Comments

Ozone and sulphur dioxide interfere.

12.12 Automatic Methods

There are no established automatic methods for the measurement of chlorine.

12.2 Source Levels

12.2.1 Manual Methods

(a) Orthotolidine

In this method gas is drawn from the stack through a probe bubbler/impinger, pump and gas meter. It can also be drawn out by use of a Standard hand pump. The principle is explained in Section 12. 1.1 (a)

Comments

Compounds which breakdown in the reagent to form free chlorine interfere.

(b) Methyl Orange Method

Sampling is performed by drawing a sample through a probe, bubbler/impinger, pump and gas meter.

The principle is explained in Section 12.1.1 (b).

Comments Interference as for 12.11 (b)

(c) Iodine - Thiosulphate Method

Gas is drawn through a probe, bubbler/impinger, pump and gas meter. The chlorine reacts with the iodine in the bubbler to form tri-iodide ion. Following collection, the free iodine is titrated with thiosulphate. The principle is explained in 12.1.1 (c).

Comments

The prescence of sulphur dioxide would cause an equivalent interference.

13. CARBON DIOXIDE

Carbon dioxide is formed in immense quantities from the combustion of fossil fuels, but is not really toxic and in this context it will not be treated as a pollutant here. However, in particulate testing of boilers and incinerators, the concentration of particulates in the gas stream is corrected to 12% carbon dioxide. This involves the simultaneous measurement of carbon dioxide.

There are a number of methods used for the determination, both instrumental and manual. However, it is important that the concentration of carbon dioxide be an integrated value for the duration of the test. For manual testing this is accomplished by taking an integrated sample and then determining the carbon dioxide concentration. For instrumental methods this task is considerably eased by recording the concentrations over a length of the test.

13.2 Source Levels

13.2.1 Manual Methods

Manual methods are all based on the collection of an integrated sample and measurement of the absorption of carbon dioxide by caustic soda or caustic pot ash. This is accomplished by the use of an)rsat analyser, Fyrite or an equivalent. In an Orsat analyser (see ref. 61) a gas sample is drawn from the integrated sample by the use of a levelling bulb till it fills an 100 ml burrette. This 100 ml of gas is then mixed with a caustic solution a few times and the resulting decrease in volume is a measure of the carbon dioxide absorbed. In a Fyrite, the gas is pumped using a small bulb into a chamber until the gas fills the space. This is then mixed with caustic and the resultant volume noted. Fyrite is much smaller than an orsat though somewhat less accurate.

The carbon dioxide concentration could also be analysed with a Gas Chromatograph and a thermal conductivity detector.

U.S, E.P.A. (See ref 17 and 18)

Gas is passed into a bag through a probe with a particulate filter and a bulb which acts as a hand pump. Alternatively, gas is passed through a probe with a particulate filter, an air cooled condensor to remove water vapout, a pump and a flow meter into a bag. The bag is slowly filled over the period of the test and then analysed by orsat or equivalent.

(b) Canadian EPS Method (See ref. 20)

This method is identical to the USEPA method.

(c) South Australian Clean Air Act Method (See ref. 19)

This method is essentially the same as the USEPA method.

13.2.2 Automatic Methods

(a) Non Dispersive Infra Red

Gas is sampled through a heated probe, a particulate filter and a condenser to remove water and measured continuously by the instrument. The principle of operation is similar to other NDIR instruments, this one being turned to absorption wavelengths of carbon dioxide. By the use of this instrument, a continuous recording for carbon dioxide is obtained and this can be used to obtain an integrated concentration over the period of the test.

Comments

This is the most reliable method of carbon dioxide measurement.

14. HYDROGEN CHLORIDE

Hydrogen chloride is a pollutant emitted by a number of industries. Metallurgical plants, ceramic industries, incinerators burning poly-vinyl chloride, pulp mills and industries using hydrocloric acid are all sources of hydrogen chloride.

14.1 Ambient Levels

There are no specific methods for the measurement of hydrochloric acid in the air although many of the methods in Section 4.1 for sulphur dioxide such as conductivity and the British Standard also measure hydrochloric acid and are not specific.

14.2 Source Levels

14.2.1 Manual Methods

(a) Gas Detector Tubes

The principal is described in Section 4.2

Comments

This method is unsuitable for accurate measurement.

(b) Potentiometric Titration Methods (See ref. 126)

Gas is sampled through a heated probe, a heated particulate filter, a bubbler of water, a pump and a gas meter. After collection the sample is titrated potentiometrically with silver nitrate giving a concentration of chloride which is then expressed as hydrogen chloride.

Comments

Other chlorides interfere.

(c) Turbidimetric methods (See ref. 126 and 127)

Gas is sampled through a heated probe, a heated particulate filter, a bubbler of water or dilute sodium hydroxide, a pump and a gas meter. After collection the chloride is precipi tated with silver nitrate in the presence of alcohol and the absorbance at 420 mm is measured.

Comments

Other chlorides interfere.

(d) Titrimetric Method (See ref. 128)

Gas is sampled through a heated probe, a heated particulate filter, a bubbler of water, a pump and a gas meter. After collection the sample is titrated with mercuric nitrate in the presence of a mixed diphenylcarbazone - bramphenol blue indicator.

Comments

Other chlorides interfere.

(e) N.S.W. Regulation Method (See ref. 16)

Gas is sampled through a heated probe, a heated particulate filter, two Greenburg Smith impingers of water, a pump and as gas meter. The dample is then analysed for acidity using a titration ofsodium tetraborate against methyl red-methylene blue indicator. Another aliquot is analysed for chloride by the tureidimetric method. Both results are expressed as hydrogen chloride and the lower result is taken as the hydrogen chloride present.

Comments

Chlorides and water soluble acids interfere only if both present.

14.2.2 Automatic Methods

(a) NDIR

An instrument turned to measure the infrared absorption of hydrogen chloride is the only automatic method available. The principle is described in Section 4.2.2a.

15. ALDEHYDES

Sources

Aldehydes are pollutants emitted from both stationary and mobile sources. Diesel powered mobil vehicles are emitters of aldehydes, the odour from these vehicles being largely due to these compounds. Coffee roasting and organic chemical industries as well as petroleum refineries are also large emitters.

15.1 Ambient Levels

15.1.1 Manual Methods

(a) 3- Methyl - 2 benzothiazolone Hydrazone (MBTH) (Ref 129, 130 and 131)

Air is drawn through a bubbler containing a solution of MBTH. The solution is then transferred to a volumetric flash, ferric chloride and acetone added and the resulting blue colour read an aspectrophotometer at 670nm.

Comments

This measures water soluble aldehydes and they are expressed as formaldehyde.

15.1.2 No automatic methods are available to measure atmospheric concentrations of aldehydes.

15.2 Source Levels

15.2.1 Manual Methods

(a) Methyl - 2 - Benzothiazolone Hydrozone (MBTH) Method (See ref. 129, 130 and 131)

Gas is drawn from the starck through a heated probe, particulate filter, bubbler of MBTH, pump and gas meter. This solution is then transferred to a volumetric flask, ferric chloride and acetone added and the resulting blue colour read in a spectrophotometer at 670nm.

Comments

Formaldehyde is the predominant aldehyde but other water soluble aldehydes are measured and reported as formaldehyde.

(b) Bisulphite Absorption Method (See ref. 132)

A large bottle is evacuated and gas is drawn from the stack through a probe, by releasing the vacuum in the bottle. The gas in the bottle is shaken with acidic silver sulphate to remove interfering gases. It is then shaken with sodium bisulphite solution and the excess bisulphite is titrated with standard iodine solution at ice water temperature.

(c) Colourimetric Method - Chromatropic Acid (See ref. 133 and 134)

Gas is drawn from the stack through a probe, bubbler of sodium bisulphite or water, pump and gas meter. The collected formaldehyde is reacted with chromotropic acid to form a purple monocationic chromagen. The absorbance of the coloured solution is red in a spectrophotometer at 580 nm.

15.2.2 Automatic Methods

(a) A flame ionisation detector as described in 7.12 can be used but it is a difficult technique to accurately calibrate for aldehydes.

There are no other automatic techniques available.

16. ODOUR

Odour sources are legion, both natural and man made. The odours themselves can be chemically simple e.g. hydrogen sulphide or complex e.g. from stock feed production. The major sources of ofour are petroleum refineries, coffee roasting, stock feed production, solvent evaporation, fermentation processes, pulp mills and rendering operations. There are a large number of minor sources and almost all process industries are a possible source of odour.

16.1 Ambient Levels

16.1.1 Manual Methods

(a) Human Nose

Frequently the human nose is the only method available to detect low levels of odour. The N.S.W. Clean Air Act makes the human nose the 'instrument" to be used for detection. Prosecution could result from the use of this "instrument".

Comments

It is subjective instrument and hard to calibrate.

(b) Gas Chromatography

This is described in Section 7.1.1 but frequently the odour is a complex mixture of compounds and they are hard to estimate collectively in a quantitive manner.

16.1.2 There are no automatic methods.

16.2 Source Levels

16.2.1 Manual Methods (See ref. 135, 136, 137, and 138)

The use of instruments to measure odour is very limited. Gas chromatography, infrared spectrometry and mass spectrometry can be used but the variability of the chemical compounds in odours restricts their use. The most widely used technique is dilution. In this method, gas is taken from the stack and diltued with odour free air in a known ration. The diluted gas is presented to human subjects who indicate whether they can detect the odour or not. When 50% of the subjects first detect the odour this is recorded as the threshold or point of detection. This method does not attempt to measure the degree of pleasantness or offensiveness of the odour, not its likely acceptability by any segment of the population.

Threshold values are used to implement air pollution control measures, based on dilution so that an odour from a source will not be detected by people outside the factory. Instruments can be used to fingerprint an odour. For example, a gas chromotographic analysis of an air sample can be matched to a threshold value obtained by dilution testing. For future odour measurement, a gas sample can then be put through the instrument and a threshold velue obtained.

However, this method is open to many errors mainly involving the change in chemical composition of the gases being emitted.

16.2.2 Automatic Methods

There are no automatic methods of measurement.

17. PEROXYACYL NITRATE (PAN'S) (SEE REF. 139)

The peroxyacyl nitrates (PANs) are a homologous series of organic nitrogen compounds that are formed when sunlight acts on air which is polluted with trace concentrations of organic compounds and nitrogen oxides. They are of particular interest because of their biological activity and apart from ozone, are some of the major end products of photochemical smog reactions.

17.1 Ambient Levels

17.1.1 Mnaual Methods

(a) Hydrolysis (See Ref 14)

The air sample is passed through aqueous potassium hydroxide which hydrolyzes PAN's to the nitrate ion. The nitrate ion is determined colourimetrically using Saltzman's reagent.

Comment

Nitrogen Dioxide interfers and therefore the method is inaccurate. However, it can be used in calibration procedures.

(b) Gas Chromotography (See ref. 140 and 143)

The analysis of PAN's by Gas Chromotography is a fairly simple procedure. Approximately 3 mls of air are injected into the column to give a relatively large response by the Electron Capture Detector. The only difficult part of this analysis is the calibration of the instrument.

This is carried out by synthesising PAN, measuring the concentration by Infra Red analysis and diluting to the required concentration.

Comment

This is very satisfactory and accurate method for the determination of PAN's.

(c) Infra-Red Spectroscopy (See ref. 139)

This is an absolute method of analysis requiring no calibration. However, at the concentrations of PAN in the atmpsphere even with 120 metre path length cells the method is at the limit of detection and so its major use is as a calibration procedure. Cost of the equipment is also high.

(d) Elemental Analysis (See Ref 142)

Using nuclear magnetic resonance spectroscopy analysis for methyl groups and neutron activation analysis for total oxygen, solutions of PAN in Carbon Tetrachloride can be analysed.

Comment

It is not as accurate as Gas Chromatography and much more complicated and expensive. It is of use as a calibration procedure.

17.1.2 There are no automatic methods of analysis, unless the gas chromatographic method is automated.

17.2 Source Levels

There are no source levels encountered in the area of air pollution.

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