

2 Air Quality and Emission Control

2.1 Significance of Man's Activity on Atmospheric Quality

In the early days of habitation of this planet, when the human population was small and its per capita consumption of energy was primarily as food (8,400-12,600 kJ/day; 2-3,000 kcal/day), total human demands on the biosphere were consequently small. Early requirements of goods were minimal and quite close to direct (requiring little fashioning) so that this early society's total demands and wastes were easily accommodated and assimilable by the biosphere, with little impact.

Today, with advances in technology providing an ever increasing range of appreciated and expected goods and services, it has been estimated that the individual consumption of energy of all forms has risen some 100-fold from the requirements of primitive man [1]. Of the one million kJ per person per day (230,000 kcal/person/day) that this collective consumption now represents, more than half, or 645,000 kJ (154,000 kcal) is estimated to be consumed by collective industrial, agricultural, and transportation needs. About a quarter is produced and consumed per person through the medium of electrical generation and consumption, either directly, for individual domestic use, or by the prorated industrial power consumption on their behalf [1]. All of the major fields of human endeavour, high technology agriculture, industrial production, and thermal electricity generation, use combustion processes to provide a major fraction of their energy requirements. When this gross increase in per capita energy consumption is coupled to a global population growth increase of a thousand or more times the population of primitive societies, it becomes easy to see how the total demand placed on the biosphere by modern industrial societies has now become so significant and evident.

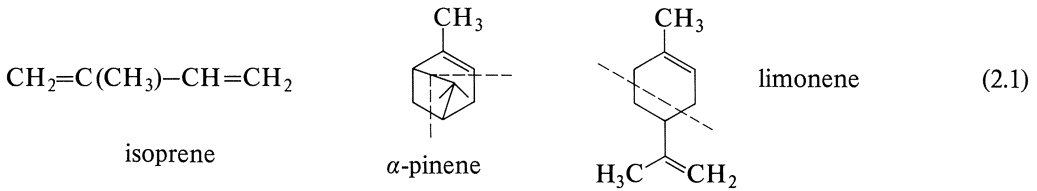
Most of the world's population growth has taken place since the Middle Ages, and the industrial development has accelerated since about 1850, so that most of the increase in demand for energy and materials has occurred during the period when

these two component increases coincided. Man's activities now contribute similar volumes of the minor gaseous constituents of the atmosphere as do natural processes. From a world fossil fuel consumption of about 5 billion tonnes per year, we now contribute about 1.5×10^{10} tonnes of carbon dioxide to the atmosphere annually [2], a significant fraction of the natural contribution, now estimated to be about 7×10^{10} tonnes/year [3, 4]. Of man's annual atmospheric contributions of sulfur-containing gases of about 10^{10} tonnes [5], of oxidized and reduced nitrogen compounds of about 50 million tonnes [6], and of carbon monoxide of about 200 million tonnes, all are estimated to be ranging in a similar order of magnitude to the natural contributions of these constituents. The old jingle "The solution to pollution is dilution" no longer holds true, particularly for atmospheric discharges. There is just too large a total mass of atmospheric contaminants being discharged, or too small an atmosphere to accept these, to still be able to discharge at the same rate and obtain sufficient dilution. This is particularly the case when natural air movement is sluggish for any reason so that little pollutant mixing occurs. Under these circumstances discharged pollutants simply remain in the same local air mass, greatly exaggerating the immediate effects of the discharge.

2.1.1 Natural Contaminants

Natural sources of many common air contaminants also make a contribution to this overall atmospheric pollutant loading. The seas contribute large masses of saltwater spray droplets to the air as a result of wave action. As the water evaporates from these droplets very fine particles of salts are left suspended in the moving air, one of the contributing factors to the sea "smell". It has been estimated that some 13 million tonnes of sulfate ion alone is contributed to the atmosphere annually from the oceans of the world [5].

Volatile organic compounds are contributed to the atmosphere by many forms of plant life, conifers such as cedar and pine, eucalyptus, and herbs such as mint. Extensive tracts of such plants, such as the



pine forests of New England, contribute a large mass of terpenes to the air above them. Terpenes, plant products biosynthetically derived from isoprene, have a type formula $(\text{C}_5\text{H}_8)_n$ based on the isoprene multiplicity of the compound (Equation 2.1).

In general all terpenes have one or more reactive double bonds so that interaction of these natural terpene vapours with sunlight and air causes a development of a photochemically-promoted blue haze over these forests during periods of little air movement [7]. Estimates of the global atmospheric contribution by plants of terpenes and oxygenated terpenes alone range from 2×10^8 to 10^9 tonnes per year [7].

The world's deserts contribute significant masses of dust and particulate to the atmosphere, some of which is transported a considerable distance. Meteoritic dust is estimated to be collected by the atmosphere to the extent of more than 900 tonnes annually [8]. However, an active volcano is a far more significant particulate contributor, some 90 million tonnes having been estimated to have been discharged into the atmosphere by the recent eruption of Mount St. Helens in Washington State [9, 10]. When several eruptions take place at one time the gross dust contribution to the global atmosphere is massive. This dust loading is generally long-lived since it is forcefully injected as high as 40 km into the atmosphere [11]. Therefore, the global influence of these events has more significance on atmospheric quality than more localized dusting events.

Sulfur dioxide and hydrogen sulfide are also contributed to the atmosphere on the scale of 1 to 2 million tonnes per year by volcanic activity [5, 12]. Other contaminating gases [13], as well as metal vapours, are also discharged in significant quantities during volcanic eruptions [14]. Emanations of the vapours of more volatile metallic elements such as mercury also occur continuously over ore bodies. Sensitive vapour detection instruments have been used as a prospecting method to converge on the ore body using this mercury vapour "halo" [15, 16].

Biological materials of many types do not represent a large mass of contamination but nevertheless comprise an important component of atmospheric pollution because of their potency. For example, very small quantities of the pollens from many types of wild flowers and grasses such as golden rod and ragweed, are sufficient to severely affect many people [17]. Bacteria, viruses, and the living spores of some of the common moulds can also cause problems, particularly when situations develop which promote a rapid, localized rise in numbers of the organism [18-20]. When this occurs in sea water, such as near sewer outfalls, dispersal of micro-organisms in the aerosols released by vigorous wave action can aggravate the problem [8, 21, 22].

Little can be done about controlling most of these natural sources of atmospheric contaminants. However, it is still important to catalogue and quantify them to be able to quantitatively relate these components of atmospheric quality to the contributions from our own activities. Only in this way is it possible to compare the relative significance of the two sources of contaminants. This is a necessary preliminary to provide informed and appropriate guidance for the modification of our own activities to decrease their negative impact on atmospheric quality where this is necessary.

2.2 Classification of Air Pollutants

Air pollutants can generally be classified into one of three main categories. By doing so, potential emissions may be grouped as to their appropriateness for one or more types of emission control devices, based on their mode of action.

The coarse particles, or the particulate class of air pollutants, comprise solid particles or liquid droplets which have an average diameter greater than about $10 \mu\text{m}$ (10^{-3} mm). Particles or droplets of this class of air contaminant are large enough that they fall out of the air of their own accord, and more or less rapidly.

Air pollutants of the aerosol class can also comprise solid particles or liquid droplets, but this time of a size range generally less than about $10\mu\text{m}$ average diameter. The important consideration for this class is that the particles or droplets are small enough in size that there is a strong tendency for the substance to stay in suspension in air [23]. Thus for the powders of denser solids, such as magnetite, the average particle size would have to be smaller than this $10\mu\text{m}$ guideline for the particle to stay in suspension. A suspension of a finely divided solid in air is referred to as a “fume”, and that of a finely divided liquid as a “fog”, each term being only a more specific representation within the aerosol classification.

The gases comprise the third major classification of air pollutants, which includes any contaminant that is in the gaseous or vapour state. This includes the more ordinary “permanent” gases, such as sulfur dioxide, hydrogen sulfide, nitric oxide (NO), nitrogen dioxide (NO₂), ozone, carbon monoxide, carbon dioxide (pollutant?) etc., as well as the less common ones such as hydrogen chloride, chlorine, tritium (³H) and the like. It also includes materials which are not ordinarily gases, such as hydrocarbon vapours, volatile non-metal or metal vapours (e.g. arsenic, mercury, zinc) when these are in the vapour state.

The dividing line between the particulate/aerosol classes, and the gaseous classes is clear enough because of the phase difference. But the position of the dividing line between the particulate and the aerosol classes, being based on whether or not a second phase stays in suspension in air, is far less obvious. However, consideration of the terminal velocities for particles of differing diameters helps to clarify this distinction. It can be seen from Table 2.1 that, for a substance with a density of 1 g/cm^3 , a significant terminal velocity begins to be observed at a particle diameter of about $10\mu\text{m}$. Hence the approximate dividing line between these two classes. Figure 2.1 gives examples of typical particle size ranges for some common industrial and domestic substances.

2.2.1 Quantification and Identification of Particulates

The particulate class of air pollutant, since it represents particles or droplets which more or less rapidly settle out of air, is also one of the easiest classes to measure. If a source particulate deter-

Table 2.1 Gravitational settling velocity for spheres of unit density in air at $20^\circ\text{C}^{\text{a}}$

Particle diameter, μm	Terminal velocity, mm/sec
0.1	8.5×10^{-4}
0.5	1.0×10^{-2}
1.0	3.5×10^{-2}
5.0	0.78
10	3.0
20	12
50 ^b	72
100 ^c	250

^a From [174 and 275].

^b Roughly equivalent to a powder which would pass through a No. 325 sieve (325-mesh, $54\mu\text{m}$ average opening size) and be retained on a No. 400 sieve (400-mesh, $45\mu\text{m}$ average opening size).

^c Roughly equivalent to a powder which would pass through a No. 170 sieve (170-mesh, $103\mu\text{m}$ average opening size) and be retained on a No. 200 sieve (200-mesh, $86\mu\text{m}$ average opening size).

mination is to be carried out, that is if the particulates in the flue gases of a chimney or the exhaust gases of a vent stack are to be sampled, then special holes are required in the ductwork. Probes with associated equipment and a means of reaching the sampling holes with this equipment are necessary. More details of this procedure are given in connection with aerosol determination.

It is also possible, however, to gain a useful quantitative record of source information by observation of the opacity of a plume. The Ringelmann system was set up by Maximilian Ringelmann in about 1890 to accomplish this for black smokes [24]. According to this system, Ringelmann numbers 1, 2, 3, 4, and 5 represent 20, 40, 60, 80, and 100 % opaque plumes respectively [8]. A circular card with shaded opacities corresponding to these Ringelmann numbers which surround a central viewing hole is available to assist in visual assessments. But a trained observer is able to reproducibly estimate plume opacity to within half a Ringelmann Number without this assistance. The obscuring properties of white smokes are specified simply on a percent opacity basis.

Another common type of particulate determination method uses the particulate fallout from ambient air as a measure of the particle loading. This method can be as simple as a series of glass jars placed in suitable areas for which dustfall measure-

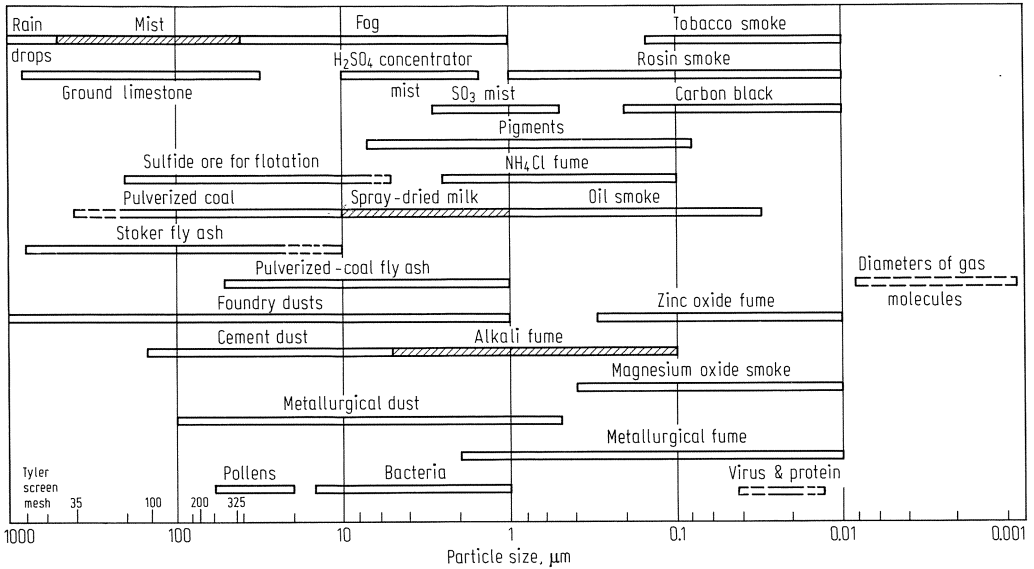


Figure 2.1. Typical particle size ranges of some types of precipitation, industrial and mineral processing streams and ambient air biologicals. From L.C. McCabe, ed., *Air Pollution*, Chap. 16 by H.P. Munger, p. 159, McGraw-Hill Book Co., New York, 1952, by courtesy of the publisher

ments are desired. The jars may be used dry, or may contain a liquid collecting agent to assist in trapping the fallout as it is collected. After a suitable interval, usually 30 days, the collected material is filtered (if wet collection was used) dried, and weighed. The weight obtained may be used to calculate a fallout value for each of the areas in which the collections were carried out. The result is specified as short tons per square mile per month, or more usually today as $\text{mg}/\text{m}^2/\text{day}$. Essentially the same procedure is used with a plastic dustfall canister on a stanchion (upright stand) specially designed for the purpose, except that a few collection refinements are used to increase the reliability of the results. The stanchion, which places the top of the canister 4 feet above the base, is also sited a reasonable distance away from trees, buildings, or roof fixtures so as to minimize the interference of fallout by anomalous air currents [25]. It is also usually fitted with a bird ring to discourage the contamination of the canister contents by birds resting on the edge of the canister itself. A further modification, a series of vertical

spikes welded to the bird ring, is necessary in areas frequented by larger species such as gulls and crows, to prevent their roosting on the edge of the canister or the bird ring.

The amount of fallout normally obtained with either device in relatively undisturbed open country is often a surprise to those who have not previously worked in the area of air pollution studies. For example, if 100 mg of dustfall is collected during a 30 day period by a glass container having a 10 cm diameter opening, this does not sound like much. But in conventional fallout units this amounts to $424 \text{ mg}/\text{m}^2 \text{ day}$, or more impressively as $36.4 \text{ tons}/(\text{mile})^2 \text{ month}$ (Equations 2.2, 2.3), actually quite a heavy fallout. Table 2.2 gives a range of some recent fallout values for the U.K. and Canada, to give a basis for comparison. The Canadian figures are somewhat high since they were obtained for an industrialized, relatively high population density area.

An early Canadian particulate guideline stipulated that no discharge was to result in a fallout exceeding 20 tons per square mile per month for any area [26].

$$(100 \text{ mg} \times 10\,000 \text{ cm}^2/\text{m}^2) \div (3.1416 \times (5 \text{ cm})^2 \times 30 \text{ days}) \tag{2.2}$$

$$(0.10 \text{ g} \times (2.54 \text{ cm}/\text{in})^2 \div (1; \text{ in}/\text{ft})^2 \times (5280 \text{ ft}/\text{mile})^2 \div (3.1416 \times (5 \text{ cm})^2 \times 9.07 \times 10^5 \text{ g}/\text{ton}) \tag{2.3}$$

Table 2.2 Average values for the particulate fallout experienced by areas of differing urban activity in the United Kingdom and Canada ^a

Type of area	United Kingdom, 1962-3 Particulate fallout		Canada, 1968 Particulate fallout	
	mg/m ² day	ton/mi ² month ^b	mg/m ² day ²	ton/mi ² month
industrial	159	13.6	233 - 350	20 - 30
high density housing	116	9.95	-	-
town center	112	9.60	210 - 256	18 - 22
town park	90	7.7	-	-
low density housing	82	7.0	117 - 163	10 - 14
suburbs, town edge	70	6.0	-	-
open country	38	3.3	82 - 140	7 - 12

^a Compiled from [174 and 276].

^b Calculated using the factor (tons/mi²/month) ÷ (mg/m²/day) = 0.08575.

2.2.2 Quantification and Identification of Aerosols

Since the aerosol class of air pollutants represent particles and droplets too small to fall out of their own accord, sampling and measurement of this class requires dynamic sampling equipment. Work has to be done on the gas to force it through the recovery or analyzing equipment so that the suspended matter can be captured. Again the analysis can be a source test, where a stack or waste vent is sampled directly, or it can be an ambient air survey, where the general condition of the outside air is determined.

Source testing requires the placing of a probe into the stack or waste vent through a sampling port in the side of the stack. A vacuum pump at the exhaust end of the sampling train provides the means for drawing the test gas sample into the train (Figure 2.2). Also important for good source

sampling technique is that the gas flow rate into the end of the probe is the same as the gas flow rate in the stack at the point being sampled, referred to as iso-kinetic sampling [27]. Otherwise some sorting of the particles sampled inevitably occurs making the results unrepresentative and unreliable [28, 29]. Also different points in the cross section of the stack must be sampled to correct for any variation in particle concentrations across a section, so-called “equal area sampling” [30]. This is necessary because, even in a long straight vertical duct, gas flow rates close to the wall of the duct will be lower, due to frictional effects. This flow rate difference, in turn, affects the relative particle loadings in the gases moving at the center, and at the edge of the duct.

As the sampled gases flow into the first series of large jets in the impactor used for collection, large particles with significant momentum strike the impactor plate, many of which remain stuck there for later analysis [31]. Smaller particles with less momentum are diverted away from this plate, still carried by the diverted current of gases. As the gases proceed further into the impactor they reach smaller and smaller jet sizes forcing the gas to move at higher and higher velocities. As the gas velocities increase, smaller and smaller particles receive sufficient kinetic energy to impinge on the collector plates, and stick there. For some kinds of test the sticking tendency may be increased by application of a thin wipe of petroleum jelly [8]. In this manner particles are collected roughly classified as to size. On completion of the test the impactor is carefully disassembled. The sorted collected material will give some information about the particle size distribution of the tested source (or

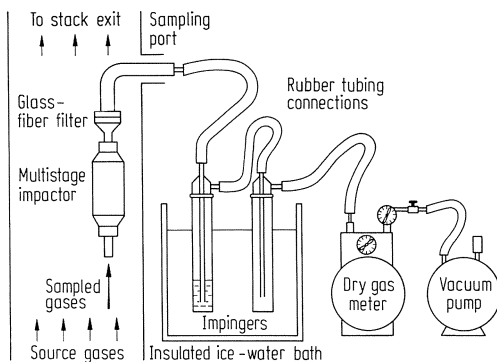


Figure 2.2. Simplified layout of an impactor sampling train [31]

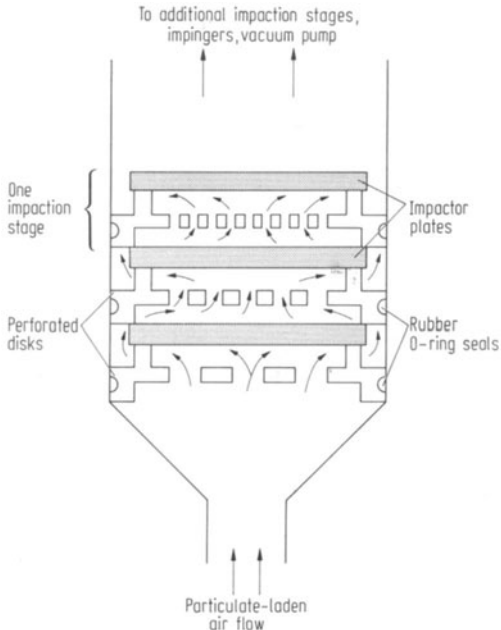


Figure 2.3. Enlarged longitudinal section of a portion of a cascade impactor for source testing [31]

ambient air). The samples are also available for other tests, such as microscopic examination [32, 33] and wet chemical or instrumental tests if desired. This system does not permit good quantitative information to be obtained, unless it is fitted with a fine pore filter (membrane or the like) for final passage of the sampled gas. A filter would, however, impose gas flow rate restrictions onto the system which in turn could limit its use for isokinetic sampling.

Filters are, however, separately useful in the sampling of ambient air for suspended matter. The high volume "high vol" sampler is one of the commonest and simplest devices used for this purpose. An air turbine driven by a vacuum cleaner motor is used to provide the suction to pull an air sample of 2,000 m³ or more through a thick 12 x 15 cm filter sheet during a predetermined test period, usually 24 hours. A recording flowmeter is used to keep track of the volume of air filtered, since the flow rate gradually declines during the test period as material collected on the filter gradually impedes air flow. The quantities (flow rate) x (time) give the volume of air filtered, and the gross weight minus the tare weight of the filter, dried to standard conditions, gives the mass collected. A quantitative

mass per unit volume result for ambient air is thus obtained, limited only at the lower end of the particle size range by the pore size of the filter used. The large particles, plus the medium to larger size range of the aerosol classification will be collected. The result is usually specified in units of mass per unit volume, e.g. mg/m³ or $\mu\text{g}/\text{m}^3$.

A refinement of the high vol sampling technique enables separation of the collected sample into coarse (2.5 to 15 μm) and fine (>2.5 μm) particle fractions with the help of different Teflon filter elements [34]. Ambient air sampling rates of about 1 m³ per hour are claimed for this device.

None of the preceding methods is very efficient at retaining particles of 1 μm diameter or less [8]. For information on this particle size range, ultrafiltration on dense cellulose or molecular membrane filters of cellulose acetate (e.g. Millipore, Isopore) is necessary [35]. Cellulose is fine for qualitative filtration work but is difficult to use in quantitative studies because of weight variations caused by the variable extent of moisture adsorption. Cellulose acetate, which is much less affected by atmospheric moisture, is also close to 100% efficient at retaining particles larger than about 0.1 μm , and has the further advantage that the filter element can be used for direct examination under a light transmission microscope for size distribution or particle identification studies [8]. The fine pore size of this filter requires a pressure differential of nearly an atmosphere to obtain adequate air filtration rates, and a good filter element support to enable the membrane to tolerate these pressures without rupture. Even using these conditions only about 0.03 m³ of air per minute can be filtered through the standard 5 cm disk [8], one of the limitations of the method.

A Mine Safety Appliance development, an analytical scale electrostatic precipitator, provides one further technique for collection of fine aerosol material, particularly useful under low loading conditions. By prior taring of the removable glass tube of this device it is possible to determine particle loadings of as low as 10 $\mu\text{g}/\text{m}^3$ after the passage of 10 m³ of air [8]. This, or even larger volumes of air may easily be sampled with this device since there is negligible resistance to air flow through the glass collection tube of this design. Identification of particles and aerosols can frequently be made using direct microscopic examination coupled with a knowledge of the collection circumstances. Particle features such as transpar-

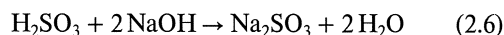
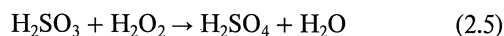
ent/opaque, colourless/coloured, rounded/angular, isotropic/anisotropic, density, and refractive index all may be determined in this way. When these properties are combined with the general visual features such as are catalogued in one of the particle atlases [36], this examination can very often be unequivocal for identification. Particles below about $0.2\ \mu\text{m}$ diameter, the limit for the best light microscopes, may be studied using electron microscopy [8, 33, 37]. Various destructive wet chemical, or instrumental techniques such as ion chromatography [38], neutron activation analysis [39, 40], or atomic absorption [41] may also be used to provide confirmation of the identities provisionally established by the visual process. Details are available from a variety of standard texts and review articles [42-46].

2.2.3 Analysis of Gaseous Air Pollutants

A wide variety of methods exists for the analysis of gaseous air pollutants within the realms of wet chemical, instrumental, and biological procedures. The analytical method of choice will depend on a number of factors among which the purpose (accuracy and number of results required), budget, equipment available, and level of training of available staff will all have a bearing. As an example of the spread of possibilities within these choices, an air (and water) pollution survey was conducted in the United Kingdom during 1972-73 which was publicized by the Sunday Times Magazine. Hardware and methods literature were made available at cost through the Advisory Centre for Education, Cambridge. The unique aspect of this survey was that it was conducted predominantly by school children. Yet it produced a set of results that has been classed as one of the most comprehensive overviews of air quality yet conducted in the British Isles.

The chief difference between the two "particle classes" of air pollutants and the gaseous air pollutants, as far as analysis is concerned, is that for the latter normal filtration methods can not be applied. Physical adsorption, such as on activated charcoal [47], or silica, or absorption into such matrices as silica gel, rubber, zeolites or the like can be used to capture many gaseous air pollutants [48]. Recovery of the gases or vapours required for later analysis, or for recycle depending on the scale, is frequently achieved by warming the bed of adsorbent or absorbent while passing air or an inert gas through

the bed. Sometimes this desorption is assisted by a pressure reduction. Wet absorption methods are also used, with a reagent dissolved in the liquid (usually water) to obtain reaction with and hence retain the pollutant of interest in the liquid as the air containing it is sparged through it. Sulfur dioxide, which is not well retained when contaminated air is sparged through water alone [49], is efficiently trapped when a solution of hydrogen peroxide or sodium hydroxide in water is used (Equations 2.4-2.6).

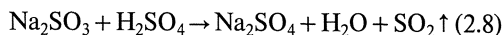


2.2.3.1 Wet Chemical Analysis of Gases

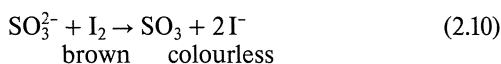
Sometimes the chemical capture reagent actually forms a part of the wet chemical analytical scheme to be used. For example, if hydrogen peroxide is used as the sulfur dioxide capture reagent, then titration using standard alkali gives the final sulfuric acid concentration obtained in the capture solution (Equation 2.5). Relating the measured acid concentration back to the original volume of air passed through the absorbing solution then gives the sulfur dioxide concentration originally present in the air. The answer obtained by this method is subject to errors when other acidic or basic gases (e.g. NO, NO₂, NH₃) or aqueous aerosols containing sulfuric acid, nitric acid, ammonium hydroxide or the like are present in the air being sampled. The influence of these interferences can be greatly decreased if the determination is carried out gravimetrically by the addition of barium chloride rather than by titration (Equation 2.7).



When sodium hydroxide in water is used as the medium to trap sulfur dioxide it allows a separate result to be obtained for the sulfur dioxide content, independent of any sulfur trioxide or sulfuric acid present in the sampled gas. This distinction is not possible when using hydrogen peroxide. To obtain this separate result requires addition of an involatile acid to the collection medium after collection. This is followed by heating, or sparging of the acidified solution with inert gas while heating, to release the sulfur dioxide from solution (Equation 2.8).



Capture of this sulfur dioxide in fresh aqueous base, followed by titration with standard iodine solution then gives the concentration of sulfur dioxide present in this second solution [50] (Equations 2.9, 2.10).



Similar wet chemical techniques have been developed for many other polluting gases, but are beyond the scope of this presentation. The general features of wet chemical analysis are such that the investment in equipment and materials required is generally low, but the skill level required of the analyst, particularly for some of the tests, is high. While it is possible to streamline some of the wet chemical methods so as to enable many results to be obtained in a working day, these methods are generally slow relative to other alternatives. Comprehensive accounts of suitable methods are available from many sources [50-52].

There is one gas analysis technique which borrows from the colourimetry of manual procedures but with which the technology of the determination is prepackaged in sealed adsorbent tubes. Draeger, and now also the Gastec and the Matheson-Kitagawa systems for gas analysis all use glass tubes packed with a solid support coated with an appropriate colourimetric reagent for the gas of interest. Company literature assesses the coefficient of variation for the tubes with most readily discernable colour changes as 10 %, and for the less efficient tubes as 20 to 30 % [53] (Equations 2.11-2.13).

This is certainly sufficient level of precision for the occasional determination of the less common

$$\text{Standard deviation} = \frac{[(x_1^2 + x_2^2 + \dots + x_n^2)/(n-1)]^{0.5}}{n}, \quad (2.11)$$

where x_1, x_2, \dots, x_n are the deviations of individual determinations from the mean of all determinations in the series being measured, and n represents the number of individual determinations in the series.

$$\text{Mean deviation} = (x_1 + x_2 + \dots + x_n)/n, \quad (2.12)$$

absolute values of the individual deviations are used, without regard to sign. It is also referred to as the average deviation.

Table 2.3 Some examples of the gases which may be determined by prepacked colourimetric tubes^a

Gas or vapour	Measurement range ^b	
	Minimum	Maximum
ammonia	5 ppm	10%
benzene vapour	5 ppm	420 ppm
carbon monoxide	5 ppm	7%
chlorine	0.2 ppm	500 ppm
ethylene oxide	5 ppm	3.5%
formaldehyde	0.5 ppm	40 ppm
hydrogen sulfide	1 ppm	7%
mercury vapour	0.1 mg/m ³	2 mg/m ³
methane thiol (methyl mercaptan)	2 ppm	100 ppm
nitrogen dioxide	0.5 ppm	50 ppm
oxygen	5%	23%
ozone	0.05 ppm	300 ppm
perchloroethylene	5 ppm	1.4%
phenol	5 ppm	c
sulfur dioxide	0.1 ppm	2000 ppm
tetrahydrofuran	100 ppm	2500 ppm
vinyl chloride	0.5 ppm	50 ppm
xylene	5 ppm	1000 ppm

^a Compiled from [53, 277 and 278].

^b Concentrations are specified by volume (see text). Wider concentration ranges are covered with two to five detector tubes of differing sensitivities.

^c Not specified.

$$\text{Coefficient of variation} = \frac{(\text{standard deviation})}{\text{mean}} \quad (2.13)$$

gases, and provides a much more convenient method for this purpose than most alternatives (Table 2.3). However, it should be noted that in the early days of the development of these systems a tube for carbon tetrachloride vapour was questioned as to its capability to achieve a precision within 50 % of stated values [54]. Nevertheless, even this level of accuracy is still adequate for many regulatory and industrial hygiene requirements.

2.2.3.2 Instrumental Methods for Gas Analysis

Instrumental analysis of air samples can frequently be conducted directly on the air or gas sample, particularly when either the concentration of the contaminant is high or when the analytical method being used is sensitive. Otherwise, prior concentration of the component of interest is necessary.

This may be accomplished by adsorption onto a substrate from low concentrations, to be later released at higher concentrations by heating, evacuation or the like. Or the concentration step may be accomplished by absorption from the air, as fine bubbles discharged under the surface of an entrapping liquid. The sampling method will be selected on the basis of the type of information required from the sample and the instrumentation that is to be used for analysis.

Spectrophotometric methods, both ultraviolet and infrared, are useful for air analysis in a wide variety of formats. Either a solution or a gas sample cell may be used. For good ultraviolet sensitivity the component of interest must have two or more double bonds present, preferably conjugated. Thus sulfur dioxide, acrolein ($\text{CH}_2 = \text{CH} - \text{CHO}$), and benzene all give very good ultraviolet sensitivity, by measurement at suitable wavelengths near their absorption maxima. In contrast acetone, phosgene, and gasoline all have direct atmospheric measurement detection limits of only about 5 ppm, too high to be useful for many situations [8]. However, even if direct measurement sensitivities are poor, a colourimetric method coupled with ultraviolet spectrophotometry may be used to obtain good sensitivity. For example, ultraviolet absorption is sufficiently more sensitive for the purple complex formed by reaction of formaldehyde with chromotropic acid than it is for formaldehyde itself to enable solution detection limits of $1 \mu\text{m}$ ($0.1 \mu\text{g/mL}$) to be achieved [55] (Equation 2.14).

For a 10 L air sample this corresponds to an ambient air sensitivity of 0.1 mg/m^3 . Ultraviolet absorption by sulfur dioxide may also be usefully applied in the field for direct plume observation. In a novel technique developed for the observation of the colourless discharge of sulfur dioxide and water vapour from a natural gas cleaning plant vent stack, use of silica optics and a special film allow the clear photographic differentiation and observation of plume behaviour [56, 57].

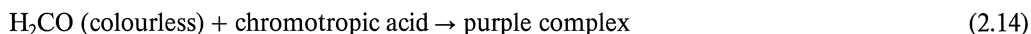
The infrared spectrum of many air pollutants is generally more complex than its ultraviolet spectrum, showing several absorption maxima. But for many single components the pattern of maxima obtained can permit positive identification of the material at the same time as obtaining the concentration from the absorbance. Any compound

absorbs infrared energy although the intensity of the absorption varies greatly from compound to compound. This affects the relative sensitivity of the method for different compounds. However, recently developed multiple path cells compensate for this somewhat by providing effective absorption path lengths of 20 m or more in a complex but compact gas cell which uses internal reflections (Figure 2.4). Typical infrared detection limits quoted for this system are 1.2 ppm for carbon monoxide, 1.5 ppm and 0.08 ppm for nitric (NO) and nitrous (N_2O) oxides, respectively, 0.1 ppm for sulfur dioxide and 0.05 ppm for carbon tetrachloride [58]. Some of these infrared instruments are conveniently portable and fitted for 12 volt power, suitable for operating from an ordinary car battery. These field capabilities avoid many of the problems faced by sample containment systems required for field collection and then transport to the laboratory for analysis.

Rapid multiple scans, signal storage, plus fourier transform capabilities have combined to push infrared detection limits to about 1/100 of the concentrations possible with these more conventional infrared instruments, but at about 10 times the cost [59-62].

The really significant spectroscopic developments that are moving air pollutant analysis into the forefront of new capabilities are closely linked to developments in laser technology [63]. The coherence and high resolution possible with a laser source, coupled with the high power available with some configurations makes inherently high sensitivities possible, particularly where the match between laser and absorbing frequencies is good. For example, it has been estimated that sensitivities of the order of 1 ppb should be possible with nitrous oxide, using a 100 m path length. Even lower sensitivities are reasonable for more strongly absorbing gases [64, 65]. The high source powers available also allow the use of lasers for remote sensing of air pollutants, such as in smog situations, or for discharge plumes, or even for ambient air pollutant concentrations [64, 66-68].

Various laser instrument arrangements are possible depending on the particular remote sensing application (Figure 2.5). The direct absorption mode, *a*, is the simplest, but suffers from the inconvenience that source and detector units must be sited separately, and aligned for each particular test situa-



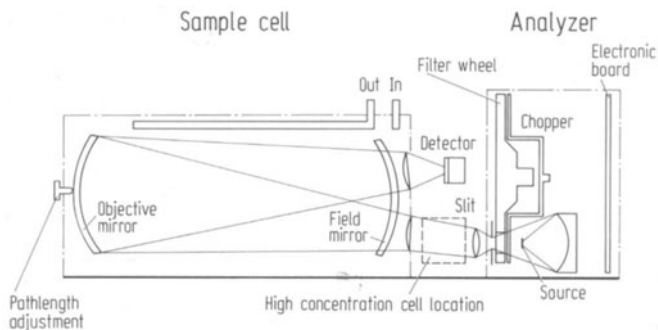


Figure 2.4. Diagram of the operating details of a portable infrared gas analyzer which uses a long path, multiple internal reflection gas cell. Adjusting the angle of the objective mirror alters the number of internal reflections obtained, before the beam enters the detector [58] (Foxboro Co.)

tion. Retroreflection, either from a surface-silvered mirror or from a geographical feature such as a tree or rock, *b*, at least allows source and receiver to be operated from the same site. In the backscatter mode, *c*, the reflections from aerosol particles which have passed through the target air sample are picked up by the receiver-detector operating at the same location. In this situation the laser is tuned to a high absorption frequency of interest and then to a low absorption frequency near this. The concentration of the component of interest may be computed from a comparison of the relative absorption signals, the basis of the so-called DIAL (differential absorption lidar) system [64, 67].

One other non-spectroscopic instrumental technique which should be mentioned as being particularly appropriate to the analysis of gaseous air pollutants is gas chromatography, particularly when this is coupled to an efficient mass spectrometer. Gas chromatographic techniques allow efficient separation and detection of many common and less common air pollutants. With the more sensitive columns and an electron-capture or similar sensitivity detector it can give a measurable signal with as little as 10^{-12} g of separated component [69]. But gas chromatography itself does not permit unequivocal identification of the separated component. Coupling a quadrupole mass spectrometer to the exit of a gas chromatograph allows both functions to be performed, the gas chromatograph to carry out separations of constituents, and the rapid acting mass spectrometer to identify them from their fragmentation patterns or molecular ions [70, 71]. The value of this combination to provide rapid answers for the real time tracking of gases, vapours, and fumes released from a train derailment emergency involving released chemicals has been well demonstrated [72-74].

Many other instrumental methods are also used for gas analysis, the details of which are available elsewhere [69, 75-77]. Development, standardization and validation of the various methods used for particular pollutants of interest are continuing and on-going processes [78, 79].

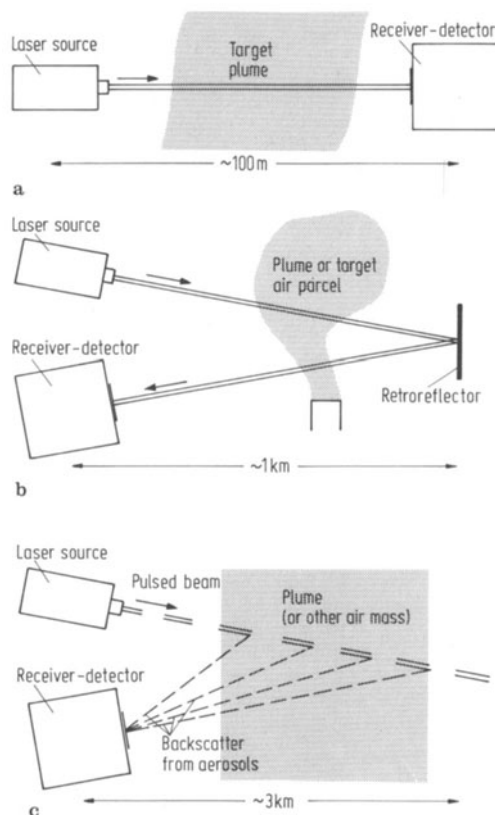


Figure 2.5. Some possible configurations of laser source and receiver detectors for use in remote sensing of air pollutants. **a** Simple direct absorption mode **b** Retroreflective direct absorption mode **c** Backscatter from aerosols mode

2.2.3.3 Concentration Units for Gases in Air

The concentration of a gas or vapour in air or any other gas phase, may be specified on a volume for volume basis, a weight for volume basis or on a partial pressure basis. Each of these concentration units has one or more features which makes its use convenient in particular situations.

Concentrations of one gas in another, specified on a volume for volume basis, are normally corrected to 25 °C and 1 atmosphere (1.01325 bar, 760 mm Hg) pressure for reporting [80]. Under this system relatively high concentrations are specified in percent (%) so that 3 % sulfur dioxide in air would correspond to 3 mL of sulfur dioxide mixed with 97 mL of air, both specified at 25 °C and 1 atmosphere. In more general terms this also corresponds to 3 parts by volume of sulfur dioxide in 100 parts by volume of the sulfur dioxide/air mixture, both specified in the same volume units. Lower concentrations are specified in smaller units, ppm for parts per million (1 in 10⁶), ppb for parts per billion (1 in 10⁹), and now that adequate sensitivity has been developed for the analysis of some air pollutants at these low concentrations occasionally even ppt for parts per trillion (1 in 10¹²) [7].

This volume for volume system of specifying gas concentrations is in essence unitless, i.e. it represents a pure ratio of quantities given in the same volume units which thus allows the units to divide out. To a chemist this system has the further advantage that comparisons made on a volume for volume basis are also on a molecular, or molar basis, i.e. a mole of any gas at normal temperature and pressure (N.T.P. or S.T.P.; 0 °C and 1 atmosphere) occupies 22.4 L. This volume for volume comparison is true for most gases and vapours when existing as mixtures at or near ambient conditions of pressure and temperature, and only deviates significantly from this molar equivalency when the conditions (pressure and/or temperature) become extreme. But it must be remembered that volume for volume data are corrected to 25 °C and 1 atmosphere, under which conditions a molar volume corresponds to 24.5 (24.46) L (298 K/273 K x 22.41 L).

These combined properties of this volume for volume concentration unit are such that, if the temperature or pressure is changed, there is no change in the concentration specified in this manner, within reasonable limits. Any correction which

may be necessary as a result of a minor variation of the measuring conditions is generally smaller than the experimental error of the analysis. Since many analyses of air samples are conducted at temperatures close to 25 °C and normal atmospheric pressure, corrections are only seldom necessary. Because of this feature the temperature or pressure does not normally need to be specified when using volume for volume units for quoting concentrations of a gas in air or another gas.

Increasingly often, however, the concentration of a gas (or vapour) in air is being specified on a weight per unit volume basis, common units for which are mg/L, mg/m³, and μg/m³ (Equation 2.14).

$$1 \text{ mg/L} = 1000 \text{ mg/m}^3 = 10^6 \text{ } \mu\text{g/m}^3 \quad (2.14)$$

Knowing the concentration of an air pollutant specified in this way allows easier determination of mass rates of emission, which are important for regulatory purposes and for exposure hazard calculations. But using this system, there is no direct molecular basis for comparison of the concentrations of any two gases, which makes it more difficult to visualize chemical relationships with this system. Also the concentration of a gas in a gas, specified in these units, changes with changes in temperature or pressure. This happens because the mass (or weight) of a minor component per unit volume in this system becomes smaller as the temperature of the gas mixture is raised, whereas the volume of the air (or other main component) in the mixture becomes larger. Both influences tend to make the specified concentration smaller with a rise in temperature. Since 0 °C has been used as "standard temperature" by some authorities [81, 82] and 25 °C by others [7, 83] for specifying weight per unit volume gas concentrations, to avoid ambiguity in specifying results in these units the temperature or the standard temperature basis used *must* also be specified. Data presented in this format are normally corrected to one atmosphere pressure.

The common usage of both volume for volume, and weight for volume units in the quoting of air pollution results frequently makes it necessary to be able to inter-convert between these units. To obtain a value in mg/m³ from a value in ppm one has to multiply the ppm value by the molecular weight in grams, of the component of interest and divide by 24.46, the molar volume at 25 °C (Equation 2.15).

The conversion process is similar for μg/m³ and

$$\text{mg/m}^3 = \frac{1/10^6 (\text{ppm}) \times \text{mol.wgt. (g/mol)} \times 10^3 (\text{mg/g})}{24.46 (\text{L/mol}) \times 10^{-3} (\text{m}^3/\text{L})} \quad (2.15)$$

$$= (\text{ppm} \times \text{mol.wgt. (g/mol)})/24.46 (\text{L/mol}), \text{ at } 25^\circ\text{C}.$$

$$\mu\text{g/m}^3 = (\text{ppm} \times \text{mol.wgt. (g/mol)} \times 10^3)/24.46 (\text{L/mol}) \quad (2.16)$$

$$\text{mg/L} = (\text{ppm} \times \text{mol.wgt. (g/mol)} \times 10^{-3})/24.46 (\text{L/mol}) \quad (2.17)$$

$$\text{ppm of constituent} = \frac{(\text{partial pressure of constituent}) \times 10^6}{(\text{total barometric pressure})} \quad (2.18)$$

mg/L from ppm, again both at 25 °C (Equations 2.16, 2.17).

For weight for unit volume values at temperatures other than 25 °C the molar volume for the temperature of interest must be used in place of 24.46 L/mole.

The partial pressure system is also occasionally used to specify the concentration of a gas in a gas (e.g. Equation 2.18).

Common pressure units are used for the partial pressure of the component of interest and total barometric pressure readings, so that the units divide out. Thus, in all important respects the partial pressure system is equivalent to the volume per unit volume system for specifying concentrations of a gas in a gas. This system is of particular value, for instance, when making up synthetic mixtures of gases on a vacuum line, where the partial pressure of each component is known, and can be used to determine the relative concentrations.

2.2.3.4 Biological Methods for Air Pollution Assessment

High concentrations of air pollutants are known to kill many annual plants and trees. This amounts to a biological indicator, albeit a coarse one. Less severe exposures can cause premature senescence (early leaf drop) of sensitive species of trees and shrubs [84, 85]. For example aspen poplar, *Populus tremuloides* drops its leaves after exposure to as little as 0.34 ppm of sulfur dioxide for 1 hour [86]. Early leaf drop slows tree growth, a measurable result which can be qualitatively determined by examining growth ring widths from tree cores [87]. The olfactory membranes, as another kind of biological indicator, also provide an odour warning of air pollutant exposure to man and many animals which in some cases rivals the sensitivity of the most sophisticated instrumentation [88]. Since many toxic gases also possess a more or less intense odour the avoidance response that a smell activates is also useful in this way [7].

However the lichens, as a group, have been far more generally useful as indicators of pollution levels over time and as measures of air pollution trends for both city [89] and rural study areas [90]. Lichens represent a slow growing symbiosis between an alga, which photosynthetically manufactures carbohydrate, and a fungus, which aids the alga in water storage in an otherwise inhospitable site and uses the manufactured carbohydrate for its own metabolism and growth. Their very slow growth, and their high reliance on the air for most of the lichens' nutrient requirements, makes for efficient uptake and retention of many air pollutants. Hence, the level of air pollution more significantly affects the growth and reproduction of lichens than that of most other, faster-growing forms of plants which rely on a soil substrate [91, 92]. Also, heavy metal fumes or other particulate air pollutant exposures tend to accumulate to higher concentrations in lichens than in most other forms of plants [87]. In the hands of skilled botanists a lichen diversity and distribution study of an area can give useful long term exposure information regarding continuous or intermittent fumigation by pollutants such as sulfur dioxide which would be difficult to obtain in any other way [93, 94].

Even in the hands of the relatively uninitiated but careful observer it is possible to determine up to 6 or 7 zones of relative air pollutant exposures by recording the diversity and types of lichens found growing in an area [95]. Thus, in a relatively polluted area few, or no healthy lichen varieties will be found. Those more resistant varieties that do occur in this exposed situation, such as *Pleurococcus* species, will be forms which are closely associated with their support and recumbent, a habit that minimizes exposure of the lichen to air pollutants. At the other extreme, in areas little exposed to air pollutants, both the species diversity and the number of specimens of each species found will be larger. There will also be a better representation of the more pollution sensitive foliose (leafy) forms

such as *Parmelia* and *Letharia* species, or the fruticose (shrubby) forms such as *Usnea* or *Alectoria* species. Biological methods based on lichen surveys such as this represent an important complement to the information obtained from wet chemical and instrumental analysis for determining the integrated levels of air pollution over time for an area.

2.3 Effects of Air Pollutants

Much has been said and written about the effects of air pollutants on plants and animals so that only a brief summary needs to be presented here. The health effects on man probably comprise the most direct, even if somewhat anthropocentric, concern with air pollutants. The primarily nuisance effect of the smell emanating from a fish packing plant represents an example at the minor end of the effects range. However, since the average person takes in some 22,000 breaths per day, amounting to some 14 to 16 kg (30 to 35 lb) of air per day [8], even a relatively low concentration of most air pollutants is sufficient in this large mass of inspired air to begin to have a noticeable effect. For this reason alone the air environment has to be the most important of the biospheric elements to be worth striving to maintain or improve in quality.

The elevated air pollutant levels which occur during localized smog episodes tend to severely im-

part on the ill, and the young and the old, causing effects all the way from excessive lachrymation and restricted breathing, to an aggravation of respiratory illnesses in particular, even to a noticeable rise in the death rate recorded for the affected area in the most severe episodes [96, 97]. London, England, the Donora valley, Pennsylvania, and the Meuse valley, Belgium, are just a few of the fairly well documented older examples of occurrences of this last level of severity [7, 98-100].

Today, two clearly differentiated types of smogs are recognized. In the classical variety of smog, represented by the pollution episodes mentioned above, the problem was caused by the accumulation of primary air pollutants such as sulfur dioxide, particulates, and carbon monoxide contributed by smoke, complicated by the presence of fog (Table 2.4). The fog also tended to slow air pollutant dispersal by cutting off sunlight, preventing the normal mixing process which is stimulated via the warming of air close to the earth's surface by the sun. The characteristics and time of occurrence of a classical smog differ markedly from the more recent phenomenon of photochemical smog which was first described for Los Angeles, but which is also experienced by Tokyo, Mexico City and other major centers with similar circumstances [101].

In photochemical smog episodes, secondary air pollutants such as ozone, nitrogen dioxide, and

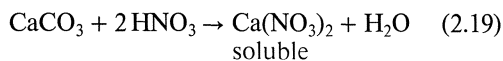
Table 2.4 Distinguishing features of classical and photochemical smogs ^a

	Classical smog	Photochemical smog
Location example	London, early	Los Angeles
Peak time of occurrence	winter	summer
Conditions	early a.m., 0 to 5 °C, high humidity plus fog	around noon, 22-35 °C, low humidity, clear sky
Atmospheric chemistry	primarily reducing, SO ₂ , particulates, carbon monoxide, moisture	oxidizing, nitrogen dioxide, ozone, peroxyacetylnitrate
Human effects	chest, bronchial irritation	primarily eye irritation
Underlying causes	fog plus stable high, surface inversion, emission dispersal of primary pollutants is prevented	sheltered basin, frequent stable highs, accumulation of secondary pollutants from photochemical oxidation

^a Compiled from [7 and 101].

peroxyacetylnitrate play the dominant role in the effects felt by plants and man [101-105]. These are formed as a result of the chemical interaction of the primary air pollutants, principally nitric oxide and hydrocarbon vapours, with sunlight and air [106]. The interesting recent development is that the authorities of the London area have been successful in reducing emissions of sulfur dioxide and particulates sufficiently via the regulations of their Clean Air Act that classical smogs are a thing of the past in this area [101]. But the more frequent and intense sunshine experienced as a result of this improvement coupled with the recent increase in automobile traffic in this city now means that London, too, occasionally experiences the irritating effects of photochemical smog occurrences [107, 108].

Air pollutant concentrations such as occur in either type of smog episode are also sufficient to affect plants more or less severely from a combination of interactions [84]. When this occurs in conjunction with mist or rain, the pH of wetted surfaces is dropped low enough to seriously damage statuary and stone or masonry buildings from a simple solution reaction of the stonework with the acidic water (e.g. Equation 2.19).



Similar processes cause the attack of ironwork and other metalwork, and accelerate the decay of exposed wood. Even aluminum, which is highly favoured for use in exterior metalwork because of its resistance to corrosion, is now showing the classic pits and erosion scars of corrosion when used in areas which have severe air pollution.

Table 2.5 Contributions of sulfuric and nitric acidity of acid rain^a

Substance	Concentration (mg/L)	Contribution to total acidity ^b
H ₂ SO ₄	5.10	57
HNO ₃	4.40	39
NH ₄ ⁺	0.92	51
H ₂ CO ₃	0.62	20
all others	ca. 0.4	ca. 12

^a Data selected from that of [110]. Determined for a sample of rain of pH 4.01 collected at Ithaca, N.Y. in October 1975.

^b Microequivalents per liter. Ammonium by titration to pH 9.0.

The lowered pH caused by rainout and washout of nitrate and sulfate from the atmosphere has also resulted in the now well known "acid rain" phenomenon (Table 2.5) [109-111]. When it is realized that a pH of as low as 2.4, about the acidity of lemon juice, or vinegar, has been measured for the rainwater of individual storms (Pitlochry, Scotland), and an annual pH value for precipitation of 3.78 has also been recorded in the Netherlands [112, 113], it is evident that this trend can only serve to further aggravate structural damage to buildings. This lowered pH of precipitation is also having a particularly serious effect on the biota of those lakes which have a limited carbonate-bicarbonate natural buffering capacity [113, 114]. When the ionic exchange capacity of soils becomes exhausted it can result in reduced growth, or actual die-back of forests [115].

Related to smogs but only relatively recently noticed by the scientific community is the phenomenon of Arctic haze, a brownish turbidity occurring in the atmosphere of Arctic regions from late fall to March or April of each year [116]. A suspended aerosol of primarily sulfates, 2 μg/m³, organic carbon, 1 μg/m³ and black carbon, 0.3-0.5 μg/m³ reduces the visibility of the region to 3 to 8 km, over an area of several thousand square kilometers and up to an altitude of about 3,000 m during this period. The novelty here is that this represents an accumulation of pollutants, remote from the original points of discharge, which by the idiosyncracies of atmospheric movements and conditions resides over and adversely influences a site not responsible for the emissions [117].

This tendency of aerosols to reduce visibility during Arctic haze episodes is also a very general effect of atmospheric particles, caused by the scattering of light by particles or droplets in the aerosol size range [7]. Apart from aesthetic considerations, high loadings of solid and liquid (fogs) atmospheric aerosols also influence flight conditions at airports, and have been implicated in rainfall promotion patterns for St. Louis [118].

Another important consideration related to atmospheric loadings and particulate size distributions concerns the potential for human effects on inhalation. The body's defences in the upper respiratory system are adequate to trap more than 50 % of particles larger than about 2 μm in diameter which are present in the air breathed. However, particles smaller than this that are not efficiently captured by the upper respiratory tract,

the “respirable particulates”, penetrate the lungs to the alveolar level [119]. Here, the more vigorous Brownian motion of these small aerosols increases their collision frequency with the moist walls of the alveoli, thus trapping a large proportion of them. This occurs in a region of the respiratory system poorly equipped to degrade or flush out accumulated material, particularly if the aerosol is inert or insoluble. Hence, any physiological effect of the presence of these foreign substances is aggravated, increasing the incidence of respiratory illness experienced in areas with high concentrations of polluting aerosols. The control efficiencies of many types of air pollution control equipment for the lower aerosol size range is poor, an important consideration when the decision is made re process emission control options [120]. Proceeding from the local and regional effects of air pollutants to the global scale, there is no doubt that our escalating use of fossil fuels coupled with the widespread cutting of forests have contributed to a steady rise in the atmospheric carbon dioxide concentration, now averaging about 0.7 ppm per year (Figure 2.6) [121-124]. Carbon dioxide is virtually transparent to the short wavelength (ca. $1\ \mu\text{m}$) maximum in the incoming solar radiation, but has a substantial absorption band in the region of the longer wavelength infrared irradiation emanating from the relatively low surface temperature of the earth. Thus, an increase in the concentration of atmospheric carbon dioxide does not significantly affect the energy gained by the earth’s surface from incoming solar radiation, because of the atmospheric absorption “window” in this re-

gion. But the carbon dioxide of the atmosphere does absorb a significant fraction of the energy in the outgoing long wavelengths, a fraction which is increasing with the increasing concentration of carbon dioxide. This net energy gain, coupled with other related influences which are sometimes collectively dubbed the “greenhouse effect”, is predicted to cause a warming trend in the earth’s climate [7, 125-129].

While the increase in average global temperatures that this thermal effect brings about may be only a Celsius degree or less, it could still cause a gradual decrease in water storage in the earth’s ice caps. This in turn could raise the world’s ocean levels, causing changes to low lying coastlines [122]. Also, an increase in average global temperatures would be likely to increase the rate and extent of desertification of marginally arable land, reducing the already limited agricultural resource. Recently, however, there appears to have been a global downturn in surface temperatures, thought possibly to arise from an increased loading of sunlight-obscuring aerosols in the atmosphere [128, 130]. Thus, consideration of atmospheric carbon dioxide concentrations in isolation is inadequate to predict overall climatic trends, even though it may be possible to predict the climatic influence of this component. Much further study and more detailed modelling of the global energy balance is necessary before the conclusions from carbon dioxide concentration trends will be any more than speculative (e.g. reference 131).

The other potential global problem from increased atmospheric pollutant levels, and of halocarbons and fixed nitrogen in particular, concerns the perceived negative influence of these gases on the stratospheric concentrations of ozone [132, 133]. This potential problem relates to the interference by these gases in the ozone-forming and degrading processes which normally contribute to the natural steady state concentration of ozone in the stratosphere. When first recognized, it was predicted that this interference would cause a decrease in the equilibrium ozone concentration present [132, 134-136]. The ozone content of the stratosphere serves as an important atmospheric filter for damaging short wavelength ultraviolet. So the net effect of a decrease in the ozone concentration was predicted to cause an increase in the global exposure to short ultraviolet which, in turn, was anticipated could cause an increase in the incidence of human skin melanomas [137]. Fortunately the apparent down-

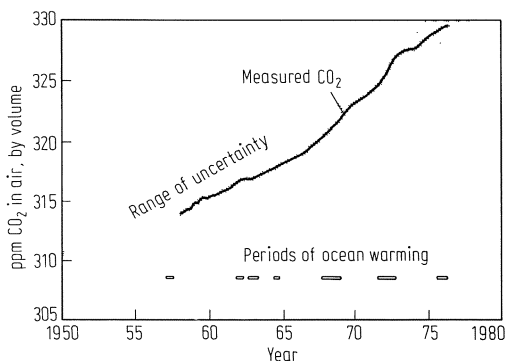


Figure 2.6. Estimated past perspectives and present trends of atmospheric carbon dioxide concentrations [122]

ward trend in atmospheric fluorocarbon concentrations in recent years resulting from voluntary use curtailment by the industry promises to minimize the influence of these effects [138, 139].

2.4 Air Pollutant Inventories, and Pollutant Weighting

In order to best apply pollution control strategies, it is an important preliminary, from a cost-benefit standpoint, to start with an inventory of the sources, mass emission rates, and types of pollutants being discharged in the area of concern. This is accomplished by a detailed analysis of the emissions from each point source of the inventory area. Data obtained by actual measurements are used wherever possible. But where measured data are not available, chemical and engineering theory is applied to come up with the best possible emission estimates within the time frame required for the inventory. Moving sources, such as automobiles, aircraft and the like are tallied by averages per unit, times the number of miles per unit, times the number of units to come up with good estimates for the contributions from these sources.

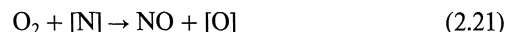
The final pollutant inventory obtained gives an overview of the total current emission picture for the study area. Table 2.6 presents this data for Los Angeles, where the inventory was conducted to assist in determining the origins/causes of the photochemical smog problem. For comparison, parallel data is presented for the whole of Canada which also has incipient smog problems in some of the major centers [140]. The best foundation for mean-

ingful planning of abatement measures, with regard to the cost and ease of control of the various alternatives relative to the extent of improvement likely to be seen from instituting these measures, is obtained from inventories of this kind.

From the tabulated data it is evident that automobiles rather than industrial activity are the source of by far the largest mass of pollutants overall (Table 2.6). Road transport, consisting of multiple moving sources under the control of individuals makes emission abatement for this classification difficult to achieve. Nevertheless, by fundamental engine design changes coupled to accessory control units installed at the manufacturing stage, significant reductions have been achieved.

2.4.1 Automotive Emission Control

As much as 70 % of the hydrocarbons, 98 % of the carbon monoxide, and 60 % of the nitrogen oxides (NO_x), have originated from the operation of automobiles (Table 2.6). Hence, these are the principal automotive emissions of concern. The hydrocarbons and carbon monoxide arise from the fact that the most power for a given engine capacity (displacement) is obtained with enough air for only 70 to 80 % complete combustion. Nitrogen oxides are formed from the interactions of atomic oxygen and atomic nitrogen, which are formed against hot metal surfaces at high temperatures, with the corresponding elements [141] (Equations 2.20, 2.21).



These emission problems are not easy to solve. To run with a leaner tuned engine (a higher air to fuel

Table 2.6 Air emission inventory for Los Angeles in November 1973 compared on a percentage basis to the annual inventory for Canada, 1974^a

Emission Source	Emissions to the atmosphere, tonnes/day					Percent of total	
	Hydrocarbons	Nitrogen oxides	Sulfur dioxide	Carbon monoxide	Totals, by source	Los Angeles	Canada
Automobiles	1 750	445	27	9 375	11 597	86.9	47.9
Organic solvent use	450				450	3.4	
Oil refining	200	41	41	154	436	3.2	27.1
Chemicals production	50		60		110	0.8	
Combustion of fuels	13	245	280	1	539	4.1	9.1
Miscellaneous	37	27	5	144	213	1.6	15.9
Totals, by pollutant	2 500	758	413	9 674	13 345	100.0	100.0 ^b

^a From [142 and 279].

^b Canadian air pollutant inventory total for the listed categories for 1974 was 25.8 million tonnes.

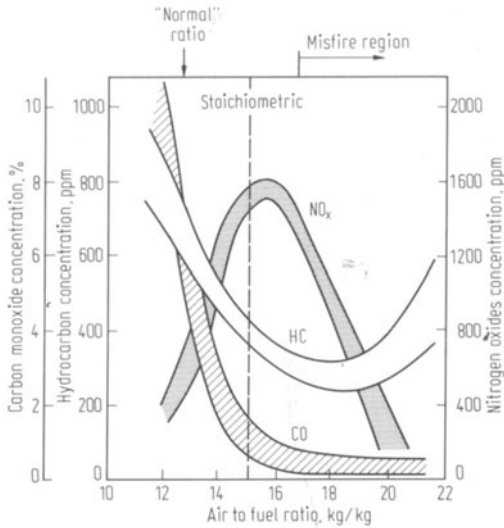
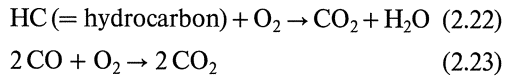


Figure 2.7. Plot of the approximate effect of various air to fuel ratios on the composition of automotive exhaust gas [142]

ratio) does obtain more complete fuel combustion and in so doing decreases the hydrocarbon and carbon monoxide concentrations in the exhaust, as would be expected. But at the same time the higher combustion temperatures obtained in the process raises the concentrations of nitrogen oxides obtained in the exhaust, and decreases the power output per liter of engine displacement [142] (Fig-

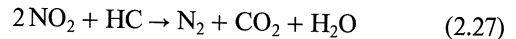
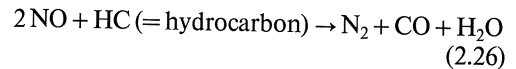
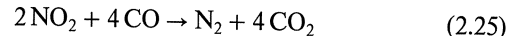
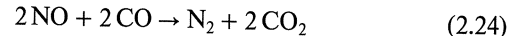
ure 2.7). It also affects driveability or smooth engine response at various throttle settings.

Early emission control methods were based on the use of a thermal reactor, for hydrocarbon and carbon monoxide oxidation, combined with exhaust gas recirculation (EGR) for reduction of nitrogen oxide emissions [143] (Figure 2.8 a). Hydrocarbons and carbon monoxide in the hot exhaust fed to the reactor, once heated, were rapidly oxidized to carbon dioxide and water by the additionally pumped air which was fed to the reactor (representative Equations 2.22, 2.23).



Some of the relatively inert exhaust gas, before it entered the reactor, was used to dilute the air fed to the carburetor by some 15 %, in so doing decreasing the peak combustion temperatures during normal engine operation [141]. This effectively decreased the concentrations of nitrogen oxides formed. These combined measures were effective in achieving significant emission reductions (Table 2.7), but at the same time caused a noticeable increase in fuel consumption and loss of performance [144, 145].

While thermal reactors have been used extensively [146], two-stage catalytic exhaust purification approached these emission problems in a different way. Here the first stage of control, NO_x reduction, is achieved catalytically using the reserve chemical reducing capacity of the residual hydrocarbons and carbon monoxide already present in the exhaust [147] (Figure 2.8 b), (e.g. Equations 2.24-2.27).



All of these NO_x -reducing reactions are much more rapid and effective than even the catalyzed direct redox reaction (Equation 2.28),



and hence accomplish most of the NO_x conversion to nitrogen. Subsequent to NO_x reduction, secondary air injection and passage of the hot mixture into

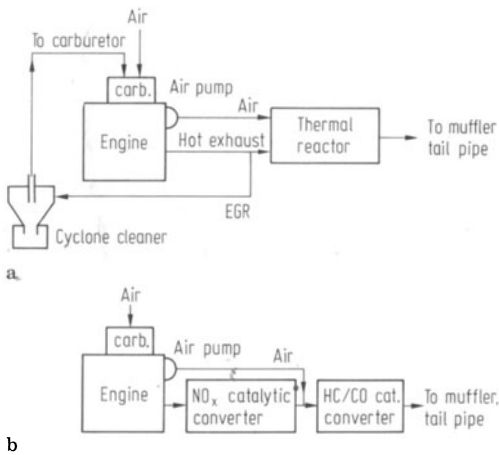


Figure 2.8. Block diagrams of two automotive emission control configurations. **a** Thermal reactor plus exhaust gas recirculation (EGR). **b** Catalytic exhaust purification

Table 2.7 Typical automotive emissions before and after regulation, related to U.S. legislated standards^a

	Grams per mile				Gasoline evapn, g/test
	Carbon monoxide	Hydrocarbons	Nitrogen oxides	Particulates	
Before control	80	11	4	0.3	60
1970 average	23	2.2	4-5	—	—
1975 standard	15	1.5	3.1	0.1	2
1980 standard	7.0	0.41	3.1	—	—
Thermal reactor + EGR ^b	4.5	0.2	1.3	—	—
Catalytic, + cyclone	0.85	0.11	1.65	0.1	1-2

^a Compiled from [142, 143, 150 and 151].

^b EGR short for exhaust gas recirculation, referring to the practice of recycling of about 10 to 15% of exhaust gases to the intake of the engine to decrease peak combustion temperatures.

a second catalytic converter accomplish complete oxidation of the residual hydrocarbons and carbon monoxide not used for NO_x reduction in the first converter [142, 148] (Equations 2.22, 2.23). One or two grams of platinum or palladium finely distributed on a ceramic matrix provides the catalytic activity of both converters [149, 150]. This combination exhaust treatment achieves better control of the hydrocarbons and carbon monoxide, and almost as good control of nitrogen oxides as achieved with the thermal reactor, and at the same time restores much of the lost fuel economy and performance [151] (Table 2.7). If a limited exhaust gas recirculation circuit is integrated with this dual converter system, the NO_x emission rate can be further improved.

Since lead-containing antiknock additives of leaded gasolines rapidly destroy the activity of the catalytic emission control system, non-leaded gasolines have to be used in automobiles fitted with this or related systems. However, since using this fuel modification also eliminates lead emissions this trend also has a highly favourable impact on the major source of lead particulate discharges to the atmosphere [152-157]. Before non-leaded gasolines were on the market it was common to find high lead levels in the core areas of busy cities [158, 159] and alongside freeways [160-163], a trend which is gradually reversing as the proportion of automobiles on the road equipped to burn non-leaded gasolines increases.

Whilst it is possible to significantly reduce particulate lead discharges from automobiles using leaded gasolines by employing cyclone-type particle collectors in the exhaust train [164-166], these methods only achieve incremental reduction, not elimination, of lead dispersal from this source.

Today, to maintain or further improve the gaseous emission characteristics of internal combustion engines the trend is towards integral improvements in engine design, such as fuel injection and various stratified charge modifications which accomplishes the chemistry of the add-on units but as an integral part of engine operation [146, 167-169]. These developments are leading to more driveable, fuel efficient automobiles.

Combinations of these control measures have resulted in a decrease in ambient carbon monoxide concentrations, and in the severity and frequency of photochemical smog incidences, where they have been applied, even though there has been a concurrent increase in the number of automobiles on the road.

2.4.2 Air Pollutant Weighting

Accumulation of emission data on a mass basis is a required step to assess the overall impact of air pollutant discharges of a region on this basis. But for development of the most effective control strategy for a control area, the contributing pollutants should be considered on the basis of their relative significance in terms of health effects, smog occurrences, and the like, and not solely on a mass basis. Two of the various weighting factors which have been proposed to do this are given in Table 2.8. While the weightings of these two systems differ significantly from each other, particularly for hydrocarbon vapours, they both assign the lowest weighting to carbon monoxide [170, 171].

If the weighting factors based on California standards are used to recalculate the relative significance of the Los Angeles emission sources on this basis, transportation still remains as the largest

Table 2.8 Examples of weighting factors used for primary air pollutants

	Weighting factors based on:	
	California ambient air standards ^a	U.S. federal secondary air quality standards ^b
carbon monoxide	1.00	1.00
hydrocarbons	2.07	125
sulfur oxides, SO _x	28.0	21.5
nitrogen oxides, NO _x	77.8	22.4
particulates	106.7	37.3
oxidants	186.9	—

^a Used as the basis of the proposed Pindex air pollutant rating system [170].

^b Based primarily on federal standards with health effect considerations [171].

single sector, but now only just larger than the combustion sources sector (Table 2.9). This treatment thus has the effect of redistributing the significance of emission control strategies among the transportation, oil refining and chemicals production, and combustion source sectors to obtain maximum effectiveness of ambient air improvement for this control area. It can be seen that a similar treatment of the Canadian data would give even higher emphasis to the industrial and power production sectors than found for Los Angeles.

2.5 Methods and Limitations of Air Pollutant Dispersal

Chimneys and vent stacks have been, and still are popular for waste gas discharge from all types of stationary sources, large and small [172]. Thermal power stations, smelters, refineries and even domestic heating appliances all use discharge and dispersal methods to dispose of their waste gases. Serious problems can arise, however, if the source is a very large one (i.e. has a high mass rate of emission) discharging into a stable air mass, particularly in the absence of control of the more noxious components of its waste gas. With the occurrence of a long term inversion a temporary shut-down of the facility may be necessary to protect public health.

Simple dispersal of the flue gases of large sources, when operated without emission controls, is becoming less and less acceptable today because of the limited capability of the atmosphere of highly industrialized regions of the globe to accept further loading. Particulate matter discharged in this way only falls out again on the immediate area, and more or less rapidly [173]. Discharged fumes, fogs, and mists too, although they are more widely dispersed, also eventually return to the earth's surface as they coagulate or coalesce into larger agglomerated particles, or are washed out of the atmosphere in precipitation. Discharged gases too, which have the best prospect of efficient dispersal, eventually return adsorbed onto, or reacted with other gases, particles, or water and also return in

Table 2.9 Comparison of actual versus weighted ^a daily air pollution inventory for Los Angeles, November 1973.

Emission source	Total mass of gaseous primary air pollutants ^b		Estimated mass of particulates and aerosols tonnes/day		Weighted mass of primary pollutant emissions ^c	
	tonnes/day	% of total	Actual	Weighted	tonnes/day	% of total
Automobiles	11 597	86.9	74	7 896	56 271	41.5
Organic solvent use	450	3.4	0	0	930	0.7
Oil refining	436	3.2	123	13 124	19 714	14.6
Chemicals production	110	0.8				
Combustion of fuels	539	4.1	245	26 142	53 108	39.2
Miscellaneous	213	1.6	27	2 881	5 371	4.0
	13 345	100.0	469	50 043	135 394	100.0

^a Weightings from California Standards, Table 2.6. See also [170].

^b Includes hydrocarbon vapours, nitrogen oxides, sulfur oxides and carbon monoxide.

^c Includes the primary gaseous air pollutants, plus particulates and aerosols.

precipitation. So a higher chimney merely spreads the combined fallout from these processes over a wider area; it does not decrease the gross atmospheric loading or fallout rate.

Multiple high chimneys in a single area tend to produce plume overlap some distance downwind of the original discharge points. This effect begins to negate the reduction in ground level concentrations of air pollutants, the original objective of the high stack (Figure 2.9 a).

If stack dispersal is to be used, it is important that the stack be sited in such a way that adjacent buildings or natural features such as hills or gullies do not serve to trap discharged waste gases close to the ground. Also to be avoided are backwash, a downdraft obtained on the leeward side of any large surface feature, or eddies which may occur in the same plane around the corners of obstructions. Any of these factors, if not allowed for, can cause plume impingement close to the point of discharge and hence cause highly elevated concentrations of the components of the discharged exhaust gases close to the ground.

A primary objective of stack discharge of waste gases is to obtain the minimum or zero elevation of the ground level concentrations of the discharged

gases in the immediate area of the stack. The stack discharge point should be high enough that sufficient diffusion of the discharged gases occurs to make the concentrations of these gases acceptable at the point the diffusion cone intersects the ground. For any given mass emission rate, Equation 2.28

$$\text{ground level concentration} = K(m/uH^2) \quad (2.28)$$

where m = mass rate of emission

u = wind velocity

H = effective stack height

may be used as a rough guide to the effect on the ground level concentration of a discharged gas which would be expected for different stack heights and wind velocities at the point of discharge [8, 174]. In this expression the “effective stack height”, corresponds to the physical stack height plus the plume rise. The plume rise is obtained from a combination of thermal (buoyant) rise and momentum rise and the height component from this factor is defined as the vertical distance between the top of the stack and the point at which the centre line of the plume levels off to within 10° of the horizontal [7]. In the case of a warm or fan-forced discharge this plume rise can add considerably to the actual stack height, significantly raising the effective height of the discharge [175, 176]. Most real situations, however, are far more complex than can be reasonably approximated using this expression, so that more complex expressions are usually required to accommodate the greater number of variables [7, 8].

The point of impingement for particulates, or the location on the ground where discharge products of the stack are at a maximum, corresponds to about 3 or 4 times the effective stack height. For gases this corresponds to about 10 times the effective stack height. Because of the influence of the “virtual stack effect”, further downward diffusional dilution of flue gases beyond the point of impingement is prevented by the presence of the ground (Figure 2.9 b). Therefore, at points further from the stack than this the concentration of any discharged gases at ground level still continues to decrease, but is found to be roughly double what would be predicted from simple diffusion cone calculations [7].

The effective height of a chimney, or the efficiency of effluent dispersion may be improved by any of a number of measures. Addition of a jockey stack, a smaller diameter supplementary stack installed on top of an existing installation, can help. Or im-

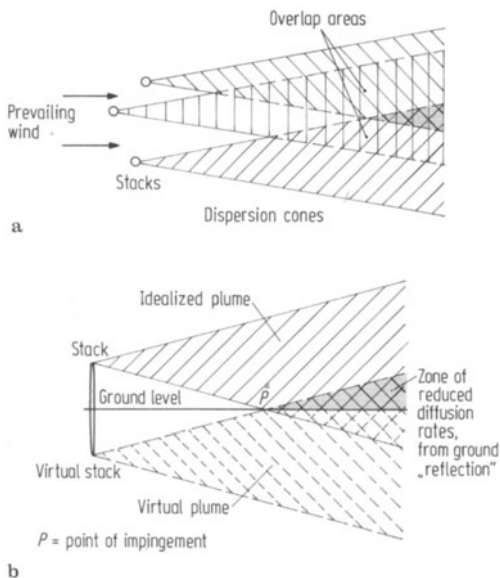


Figure 2.9. Horizontal(a) and vertical sections(b) of stack discharges showing how overlapping plumes, and virtual stack effects increase ambient air concentrations of pollutants at ground level above that to be expected from simple diffusion cone calculations

provement may be gained by raising the flue gas temperature or velocity to obtain greater plume rise. Valley inversions may be avoided by running ductwork up a hillside for discharge via a stack at the top, taking advantage of both the increased height above the inversion layer and the higher windspeeds for more efficient dispersal [177]. Diffusion and dispersal rates under stable air conditions may also be improved by the use of vortex rings [178], or super high stacks [179, 180]. But ultimately, particularly with very large installations discharging in areas where inversions are frequent, containment measures of one sort or another in conjunction with stack discharge have to be considered [181].

2.6 Air Pollution Abatement by Containment

With the increasing dilution and dispersal burdens being placed on a finite volume of atmosphere it is becoming more and more clearly evident that containment, or neutralization of air pollutants is required before discharge in order to prevent further deterioration in air quality [115, 182]. Air emission control measures which fall into this category may be precombustion or predispersal measures, which clean up a fuel or combustion process or modify a chemical process in such a way that the pollutant of concern is never dispersed into the exhaust gases. Or they may comprise measures taken to remove or neutralize the particulates, aerosols, and gases to be discharged *after* the combustion or chemical processing step. The choice of which action or combination of actions to be taken in any particular case depends on whether the process is already in operation or in the planning stage for construction, and the type of pre- or post-combustion emission control strategies which are available or may be readily developed. These options are each discussed separately.

2.6.1 Pre-combustion Removal Methods

If the technology is accessible and the cost of applying it is not too great, pre-combustion removal

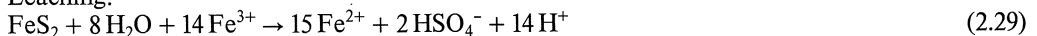
of potential air pollutants has a great deal of merit [183]. At this stage not only is the offending substance (or substances) present in the highest concentration but it has not as yet been dispersed into the combustion or process exhaust gases.

For example the incombustibles in coal, which can contribute significantly to the particulate content of the flue gases on combustion (as well as to the bottom ash volume), are now removed before combustion for more than half of the coal produced in North America [8]. This is accomplished by using one or more of the following cleaning methods with coal that has been previously finely ground [184, 185]. It may be washed with water on riffle boards, during which the less dense coal particles are carried by the water stream while the more dense rock particles tend to sink and are captured in the cavities. In air jigs the powdered mixture is suspended on a bed of air in a fluidized form. In the jig the heavier rock particles tend to sink and may be drawn off the bottom, and the cleaned coal is drawn off the top. Or an actual liquid or fluidized dense solid may be used to obtain a more direct sink-float or froth flotation separation of the coal, of density about 1.5 g/cm³, from the denser rock particles and other impurities.

In the process of the pre-combustion cleaning of powdered coal a significant proportion of the sulfur is also removed. Since about half of the sulfur compounds present in uncleaned coal reside in inorganic pyrite and sulfates, and about half in organic sulfur compounds present in the coal, it is much of the inorganic sulfur that is removed by the particulate cleaning methods [186]. This level of improvement can be further increased to some 80 % or so of the total sulfur present by using various aqueous leaching chemicals such as ferric sulfate [187-189] or sodium hydroxide [190], in the coal cleaning procedure, or by extraction with an organic solvent such as molten anthracene, *after* conventional coal cleaning [191-193] (Equations 2.29, 2.30).

Microbial methods of coal desulfurization have also been tested [194]. By precombustion cleaning measures such as these the emission characteristics of coalburning installations may be dramatically

Leaching:



Regeneration of leach solution:



improved. Coal conversion to a liquid or gaseous fuel permits much greater improvement in the residual pre-combustion impurities present [195-198], but also at greater cost [199].

The same kinds of considerations apply in the pre-combustion emission control measures used for the non-distilled fractions of petroleum, the residual fuel oils, which are used as utility fuels. The residual fuel oils contain all of the involatiles of the original crude oil, concentrated by a factor of 6 to 10 times since the volatile fractions have been removed. As a result, these fuels possess a significant potential for particulate and sulfur oxides emission on combustion. Normal refinery crude oil desalting practice is capable of removing 95 % or more of the particulate discharge problem before the crude is ever distilled [8]. But to lower the sulfur dioxide emission requires either use of only low sulfur crude oils for residual fuel formulation [200, 201], or more complicated and expensive catalytic de-sulfurization processing of the residual feedstocks prior to formulation as a fuel [201-204]. Even the volatile petroleum fractions present in natural gas, principally methane and ethane, are not without their sulfur gas polluting potential if burned directly in the state in which it is obtained from the well head. But this is normally thoroughly de-sulfurized using an amine scrub before it is piped to industrial and domestic consumers as another pre-combustion cleaned fuel [205, 206]. More details of this process are given later.

2.7 Post-combustion Emission Control

2.7.1 Particulate and Aerosol Collection Theory

Of the two non-gaseous air pollutant classifications, particulates and aerosols, the aerosols are much more difficult to control because they do not readily settle out of a gas stream of their own accord. The separation of aerosols from a waste gas stream is however greatly improved if the very small particles or droplets are agglomerated (coagulated or coalesced) to larger particles or drops, before removal is attempted. There are four primary means by which the agglomeration of aerosols can occur. Being aware of these contributing factors can provide a useful background to enable measures to be taken to accelerate the process. Brownian agglomeration, an important contribut-

ing process to the natural removal of aerosols from the atmosphere, is the first of these. The microscopic particles of fumes and fogs are so small that the frequent collision of gas molecules with them causes them to move in an erratic path, commonly called Brownian motion. When this occurs with reasonably high concentrations of aerosol particles, i.e. high particle *numbers*, it results in frequent particle particle collisions. Particle collisions usually result in agglomeration by poorly understood mechanisms, forming loose clusters or chains with solid particles and larger drops with liquid droplets. The coagulation rate for any particular aerosol system is predictable to a significant extent [8] (Equation 2.31).

$$\text{Coagulation rate} \rightarrow K_b c^2, \text{ where} \quad (2.31)$$

K_b is the rate constant for Brownian coagulation of the particular type of particle, and
 c is the number of particles per cm^3 .

The coagulation rate is seen to be proportional to the square of the particle concentration, making the number of particles per unit volume the single most important factor affecting the rate of Brownian coagulation. Table 2.10 not only illustrates this aspect, but also gives the indication that concentrations of aerosols above about $10^6/\text{cm}^3$ are unstable, and concentrations above this will rapidly drop to near this concentration range by agglomeration processes. As particles larger than ca. 5-10 μm form, i.e. in the particulate rather than the aerosol size range, they are removed by sedimentation. It is a combination of processes such as these which contribute to keeping the aerosol concentration in

Table 2.10 The relationship of coagulation time to the original particle concentration ^a

Initial concentration of particles per cm^3	Time for the number of particles to be decreased to $1/10$ initial conc.
10^{12}	0.03 sec
10^{11}	0.3 sec
10^{10}	3.0 sec
10^9	0.5 min
10^8	5.0 min
10^7	50 min
10^6	8.3 hours
10^5	17 hours
10^4	1.3 days

^a Data cited and extended by calculation using the methods given in [8].

the earth's atmosphere in the range below about 10^4 to 10^5 particles per cm^3 [7].

Turbulent coagulation occurs when particles in multiple flow line intersections collide, a process stimulated by turbulent flow, or eddy conditions. The turbulent coagulation rate is again proportional to the square of the particle concentration [8] (Equation 2.32).

$$\text{Coagulation rate} = K_s c^2, \text{ where} \quad (2.32)$$

K_s is the rate constant for turbulent coagulation.

The magnitude of K_s , the proportionality constant for turbulent coagulation, is in the range of 10 to 4,000 times K_b . Hence, turbulent coagulation can be used to greatly accelerate the natural agglomeration processes useful for emission control.

In natural situations, such as when burning wood out-of-doors, a smoke containing 10^6 particles/ cm^3 may be generated. By a combination of Brownian and turbulent coagulation processes the average particle size in this smoke can increase from $0.2 \mu\text{m}$ to $0.4 \mu\text{m}$ before it has travelled 1,000 m [8].

Sonic agglomeration applies to the use of high intensity sound waves to accelerate particle coagulation [207]. This procedure is based on the premise that particles of different sizes will tend to vibrate with different amplitudes, increasing the opportunities for collision and coagulation [8]. Also, the particle concentration in the compression zone of a high intensity sound wave will temporarily be raised, artificially increasing Brownian coagulation rates. Applying this technique involves the exposure of a particle-laden gas stream for a fraction of a second to a high intensity siren or oscillation piston, operating at 300 to 500 Hz and 170 decibels in a sound insulated chamber [208]. After exposure the particulate collection efficiency of downstream containment devices is significantly improved from the greater proportion of large particles produced. Electrostatic methods, the fourth class, may also be used to obtain efficient coagulation of particles of the aerosol size range and larger. By passing a particle-laden gas stream past the negative side of a high D.C. voltage corona (intense electric field), the particles become negatively charged. They are then efficiently attracted and coagulated against positively charged plates which are in close proximity. Periodic rapping of the plates or a trickle of water dislodges the large particles into collection hoppers. People involved with stack sampling of

gases downstream of an operating electrostatic precipitator should remember that the 20,000 to 30,000 volts normally used is high enough to leave a hazardous residual charge in the very small fraction of particles not retained by the precipitator.

2.7.2 Particulate and Aerosol Collection Devices

Gas cleaning devices vary in their removal efficiencies, but almost invariably are more efficient at removing particulate, rather than aerosol size range material. But even the least efficient device for removing small particle sizes, the gravity settling chamber (Figure 2.10), still plays an important role in emission control. When the gas stream to be cleaned has only large particles present which can be effectively removed by the device, then this device alone represents an inexpensive method of control. When the particle size range to be collected is wide, and a dry cyclone is to be used for final particle collection, very large particles (100 to $200 \mu\text{m}$) *should* be removed prior to the gas stream entering the cyclone. Otherwise the interior of the cyclone is subjected to very high abrasion rates.

Since the efficiency of gas cleaning devices is almost inevitably better for larger particles than for small and since the number of particles represented by any given mass goes up exponentially as the particle size goes down, mass removal, rather than particle removal efficiencies have become the standard method of specifying air cleaning capabilities. In one example, a particulate control device with a 91 % mass efficiency worked out to have only 0.09 % particle count efficiency for the same hypothetical dust-laden gas sample [28]. Thus, to be fully aware of the collection characteristics of an air cleaning device one must have both mass removal efficiencies, plus the particle size range over which the mass removal efficiency was measured [201]. Typical characteristics of a number of particle collection devices have been collected in Table 2.11.

The operating characteristics of some common particulate emission control units are illustrated in Figure 2.10. Cyclones, which are extensively used in industry for this purpose, are most efficient in small diameters which forces the entering gas stream through higher tangential velocities. It is high tangential velocities which most efficiently separate particles from the gas. To obtain the same

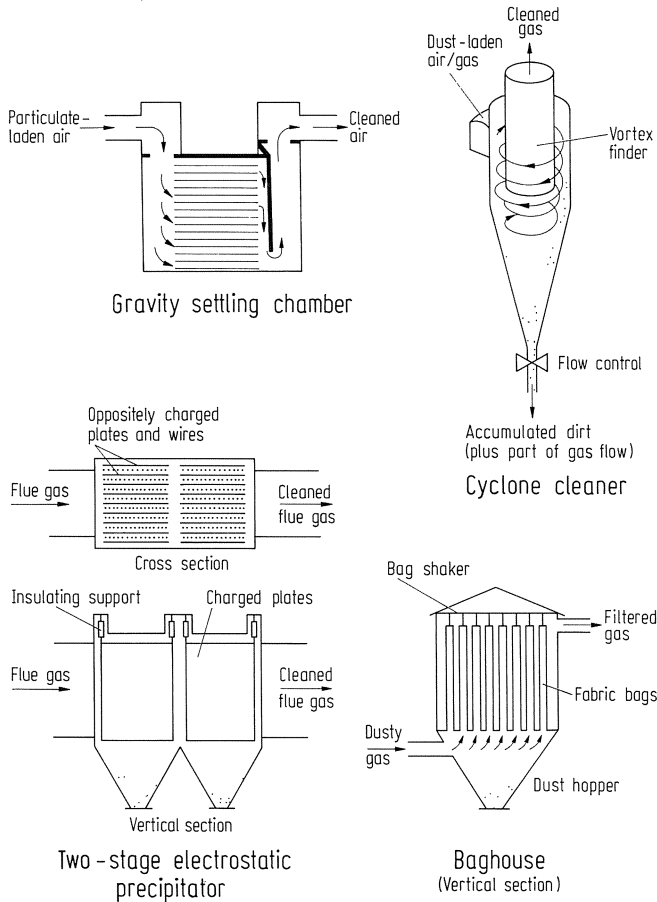


Figure 2.10. Simplified diagrams of some of the common types of particulate and aerosol emission control devices. Some of these are also useful for gas or vapour emission control. See text for details

Table 2.11 Examples of typical collection efficiencies for some common types of particulate and aerosol gas cleaning devices^a

Air cleaning device	Particle size range for 90% removal, μm	Remarks
Gravity settling chamber	50 - 100	effective only at low gas velocities, < 200m/min
Baffle chamber	20 - 100	gas velocity ca. 300 m/min
Dry cyclone	10 - 50	gas velocity 300 to 1500 m/min 2 - 750 cm diameter, smaller are more efficient
Spray washer	5 - 20	gas velocity 70 - 100 m/min
Packed tower scrubber	1 - 5	gas velocities to 4000 m/min
Intensive rotary scrubber	0.1 - 1	high resistance to gas flow (pressure drop)
Cloth filter	0.2 - 1	used in bag houses or continuous roll filters
Absolute filter	0.01 - 0.1	highly efficient but considerable resistance to flow
Electrostatic precipitator	0.01 - 10	must have low gas flow rates, very low pressure drop, very large units (> 3000 m ³ /min)
Activated charcoal	molecular	normally for control of gases, vapours, and odours; also retains particles, about as cloth filter

^a Compiled from data in [7, 8, 28 and 280].

high efficiencies with very large gas volumes a large number of small cyclones are connected in parallel, rather than using a single, very large cyclone.

Absolute filters, developed by the U.S. Atomic Energy Commission for containment of radioactive particles, are extremely efficient for retention of very fine particles but require considerable operating energy because of a large pressure drop across the filter element.

Electrostatic precipitation is also very efficient for retention of very fine particles, as long as these are not highly electrically conductive. But the structural features of these units are such that they are only cost effective for particulate and aerosol emission control for very large volumes of gas, hence their typical use in fossil-fueled power plants.

2.7.3 Hydrocarbon Emission Control

Adoption of automotive control devices has had the most significant effect on the gross hydrocarbon emissions for regulated areas, because of the large contribution to the total mass of hydrocarbons originating from this source (Tables 2.6, 2.7). But this measure on its own will not necessarily be effective for photochemical smog abatement since it is the reactive hydrocarbons, rather than total hydrocarbons which are of greatest significance [210, 211].

Measures which can reduce the ventilation losses of hydrocarbons from the tank farms and other points of an operating oil refinery are discussed with the technology related to this industry, Plate 2.1.

In the drycleaning business or in vapour degreasing plants, losses of hydrocarbon, or chlorinated hydrocarbon vapours occur from the use and re-

covery of solvents. These losses can be prevented by the use of activated adsorbent systems to capture the organic vapours from the vents or hoods of these devices [212]. Activated carbon, which is available in versions providing up to 1,000 m²/g (ca. 8 acres/oz) of adsorption area is one of the best adsorbents for this purpose because of its selectivity for organic vapours. Solvent present in high concentrations in air may also be recovered by cooling the air to liquid nitrogen temperatures to condense the solvent [213].

Air contaminated with low concentrations of organic vapours, which can also arise from a number of processes, may be economically controlled by using this air stream as boiler feed air. Any combustibles present are burned to provide fuel value, in the process destroying any hydrocarbons present before discharge [214, 215]. This method is particularly appropriate when the concentration of organic vapours in air is too small for economic containment using adsorption [216, 217].

The paint industry, with its high dependence on solvents and active, filmforming components some of which come into the regulatory "reactive hydrocarbon" class, has also been hard pressed to meet air quality tests [218-220]. But by the further development of water-based coatings, even for many metal-finishing applications [221-223], and by innovations into such areas as high solids, or even dry powder coating technologies the industry is decreasing its dependence on organic solvents for many finishing applications [224-226]. In turn these measures have decreased the emission of hydrocarbons when the coating is applied, and when combined with electrostatic application technology to better direct the coating particles or droplets onto the surface being coated these techniques simultaneously result in much less wastage as well.



Plate 2.1. Floating roof petroleum storage tank for the control of hydrocarbon vapour loss. Roof is sunk below the rim of this partially empty tank, shown by inclined service walkway.

2.7.4 Control of Sulfur Dioxide Emissions

Total sulfur dioxide discharges for the U.S.A. for 1981 amounted to 22.5 million tonnes [227]. Combustion sources concerned with power generation produced about 60 % of this, and a further 37 % was evenly split between other stationary combustion sources (mainly space heating) and industrial processes [228]. More than half of that originating from industrial processes, or about 11 % of the total, arose from the smelting of sulfide minerals and metal refining activities. Only about 3 % of the total originated with the transportation sector.

The extent of sulfur dioxide emission is of importance for the direct effect it has on the ambient air levels, for which guidelines have been laid down to protect public health (Table 2.12). However, the atmospheric half life of discharged sulfur dioxide is estimated to be short, of the order of 3 days [229]. This rapid return of sulfur dioxide to the earth's surface, both as sulfur dioxide itself [230] and as its oxidized and hydrated products is the reason for its significance as a contributor to the acidity of rainfall, about which comment has already been made [109-113]. "Sulfurous acid", from hydrated sulfur dioxide, and sulfuric acid, formed from the oxidation of sulfurous acid or the hydration of sulfur trioxide, both contribute to low pH rain. Sulfur trioxide forms through the gas phase and heterogeneous oxidation of sulfur diox-

ide on particulate matter, which occurs to a significant extent both in plumes and in the ambient air [231-233].

The industrial origins of two of the major sulfur dioxide discharges, combustion sources, and sour gas plants (in Canada) generally produce waste gas streams containing 0.15 to 0.50 % sulfur dioxide, too low to be economically attractive for containment. Only with the smelter sources, which commonly produce roaster exhaust gas streams containing 2 to 5 % sulfur dioxide and with modern equipment up to about 15 % sulfur dioxide, is it anywhere near an economic proposition to contain the sulfur dioxide. This will either be sold as liquid sulfur dioxide, or converted to sulfuric acid for sale. The smelter acid product, being less pure than sulfuric acid from sulfur burning sources, commands a much lower market price but is still a useful grade for such applications as metal pickling and the manufacture of fertilizers.

A number of solutions exist for decreasing the sulfur dioxide emissions from sources where the concentrations present are too low for economic containment. The choice in any particular situation depends on the existing ambient air quality (particularly with regard to public health) in the operating area, and the time frame within which abatement action has to be taken.

Temporary shutdown or a reduced level of operation may be required of a fossil-fueled power sta-

Table 2.12 Ambient air quality standards for Canada and the U.S.A., given in $\mu\text{g}/\text{m}^3$ and parenthetically in ppm^a

Pollutant	Averaging time	Primary standards (Health related, or maximum acceptable)		Secondary standards (Welfare related, or maximum desirable)	
		Canada	U.S.A.	Canada	U.S.A.
Total suspended particulate	annual ^b	70	75	60	60
	24 hour	120	260	—	150
Sulfur dioxide	annual ^c	60 (0.02)	80 (0.03)	30 (0.01)	—
	24 hour	300 (0.11)	365 (0.14)	150 (0.06)	—
	3 hour	—	—	—	1300 (0.50)
Carbon monoxide	1 hour	—	—	450 (0.17)	—
	8 hour	15 (13)	10 (9)	6 (5)	10 (9)
Nitrogen dioxide	annual ^c	100 (0.05)	100 (0.053)	60 (0.03)	100 (0.053)
	24 hour	200 (0.11)	—	—	—
Ozone	24 hour	50 (0.025)	—	30 (0.015)	—
	1 hour	160 (0.08)	235 (0.12)	100 (0.05)	235 (0.12)
Lead	3 month	—	1.5	—	1.5

^a Compiled from [227 and 281].

^b Annual geometric mean.

^c Annual arithmetic mean.

tion or smelter to avoid producing local, dangerously high ambient concentrations of sulfur dioxide during a severe, inversion—promoted smog situation. Over a longer time frame temporary curtailment requirements of this kind may be anticipated, by a power station for instance, by having separate stockpiles of low-cost, relatively high sulfur content coal for periods of power generation during normal atmospheric conditions, and alternative more expensive lower sulfur coal (or even coke, or natural gas, if suitably equipped) which may be burned during severe inversion episodes. With this latter option available emission curtailment by reduction of power production or temporary shut-down, which can be quite costly and inconvenient alternatives, will be required less often. Emission reduction measures which have greater

lead times to institute involve process modifications to avoid generating the sulfur dioxide-containing waste gases. For smelters this might mean adoption of hydrometallurgical technology such as is now available for copper, nickel, and zinc, in order to bypass the older roasting methods of sulfur removal from ores [234-237]. For power stations this option might mean the installation of more rigorous pre-combustion sulfur removal techniques for their coal or residual fuel oil, or increased emphasis on natural gas firing, or selection of hydro-electric, nuclear, or solar-related technologies in the utility's long term plans for power generation.

A third choice to a company faced with a need to practise emission reduction is to remain with the existing front end process, which continues to

Table 2.13 The chemical details of some examples of stack gas desulfurization processes^a

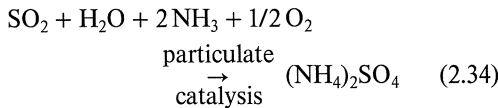
Reaction phases	Process examples	Regeneration method	Product(s)
<i>Gas-gas</i>	Homogeneous:		
	– gaseous ammonia injection plus particle collection	none	(NH ₄) ₂ SO ₃ , (NH ₄) ₂ SO ₄
	Heterogeneous:		
	– SO ₂ reduction with H ₂ S + catalyst (Claus)	none	S
	– SO ₂ reduction with CH ₄ + catalyst to H ₂ S, then amine scrub (e.g. Girbotol), or aqueous AQ (Stretford) recovery ^b	none air	conc. H ₂ S S
	– SO ₂ catalytic oxidation with air (chamber, or contact processes), plus hydration	none	H ₂ SO ₄
<i>Gas-liquid</i>	Absorption, plus chemical reaction:		
	– by aqueous ammonia solution	none	(NH ₄) ₂ SO ₃ , (NH ₄) ₂ SO ₄
	– dimethylaniline solution (ASARCO)	heat	conc. SO ₂
	– aqueous sodium sulfite (Wellman-Lord)	heat	conc. SO ₂ , Na ₂ SO ₄
	– citrate process, U.S. Bureau of Mines	H ₂ S	S
	– citrate process, Flakt-Boliden version	heat	conc. SO ₂
	– eutectic melt(Na ₂ CO ₃ /K ₂ CO ₃), gives dry plume	water gas	conc. H ₂ S
– limestone (or lime) slurry scrubbing, inexpensive, throw-away slurry product	none	CaSO ₃ · n H ₂ O, CaSO ₄ · 2 H ₂ O	
<i>Gas-solid</i>	Physical adsorption:		
	– SO ₂ onto activated charcoal or alkalized alumina	heat	conc. SO ₂
	Adsorption, plus chemical reaction:		
	– powdered limestone injection, 20 – 60% efficient capture with particle collection (precipitator), waste product	none	dry CaSO ₃ , and CaSO ₄
	– CuO (or other metal oxides)	methane	conc. SO ₂
Chemical reaction:			
– SO ₂ reduction in heated coal bed, Resox process	none	S	

^a Compiled from sources cited in the text, where further details are available, plus the reviews of [228, 242, 282 – 285].

^b AQ, short for anthraquinone disulfonic acids, see text for details.

produce a sulfur dioxide-containing waste gas stream, and move to some system which can effectively remove the sulfur dioxide from this waste gas before it is discharged. Many methods are available, each with features which may make one of them more attractive or suitable than the others for the particular sulfur dioxide removal requirements of the process (Table 2.13). Some of the factors to be considered in arriving at an appropriate process choice are the waste gas volumes and sulfur dioxide concentrations which have to be treated and the degree of sulfur dioxide removal required, remembering that the trend is towards a continuing decrease in allowable discharges. Further considerations are the type of sulfur dioxide capture product which is produced by the process and the overall cost of it, considered with any product credit which may help to decrease process costs. Finally the type of controlled gas discharge required for the operating situation, i.e. warm or ambient temperature, moist or dry etc., also has to be taken into account. Chemical details of the processes of Table 2.13 are outlined below.

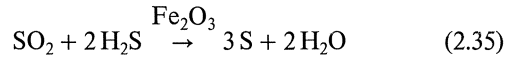
Only one control procedure, ammonia injection, relies solely on gas phase reactions. The moist flue gas containing hydrated sulfur dioxide undergoes a gas phase, acid-base reaction to produce particulate solids (Equations 2.33, 2.34).



The solid product, now a separate phase, can be readily captured by electrostatic precipitation or any other particulate collection device which is already normally in place for fly-ash control.

Heterogeneous reduction processes still involve the reaction of gases, but in these cases the reaction oc-

curs in the presence of a suitable solid phase catalyst. Sulfur dioxide may be reduced to sulfur with hydrogen sulfide, if this is available, and the sulfur vapour condensed out of the gas stream by cooling, the second half of the Claus process [238, 239] (Equation 2.35).



Or the sulfur dioxide may be reduced catalytically with methane or other hydrocarbons to hydrogen sulfide [240]. The hydrogen sulfide produced by this method is captured by amine scrubbing of the reduced gas stream (Equations 2.36-2.38).

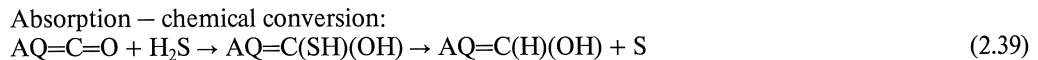
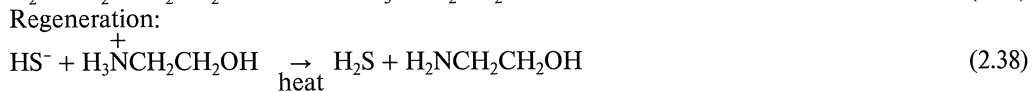
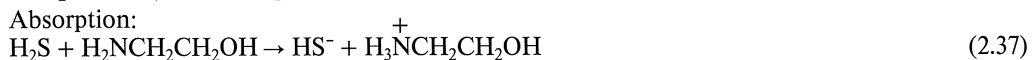
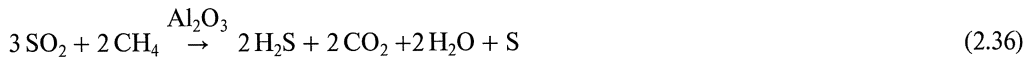
The high concentration of hydrogen sulfide obtained by heating the amine salt may then be easily and economically converted to elemental sulfur via the Claus process. The Stretford process, which may also be used for hydrogen sulfide capture, accomplishes both capture, using an aqueous mixture of 1,5- and 1,8-disulfonic acid of 9,10-anthraquinone (AQ), and conversion of the hydrogen sulfide to sulfur in a single step [241] (Equation 2.39).

Regeneration of the quinone from the quinol is accomplished with air (Equation 2.40).

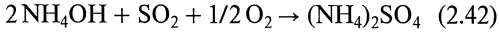
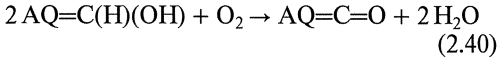
Heterogeneous catalytic oxidation of sulfur dioxide with air, via the contact or the chamber process, so serves to improve the collection efficiency of the sulfur oxides. Sulfur trioxide has a very strong affinity for water, unlike sulfur dioxide [49, 227], so that collection of sulfur trioxide by direct absorption into water is extremely efficient, and the product sulfuric acid is a saleable commodity.

Sulfur dioxide containment by gas-liquid interactions can be as simple as flue, or process gas scrubbing with dilute ammonium hydroxide [242] (Equations 2.41, 2.42).

The ammonium salt products crystallized from the concentrated spent scrubber liquors may be used as



Regeneration:



valuable constituents of fertilizer formulations. Or they may be first reduced to ammonia and hydrogen sulfide with natural gas, followed by conversion of the hydrogen sulfide to sulfur by a Claus-type sequence [243, 244]. In this French designed modification, the ammonia is recycled to the scrubbing circuit.

Similar acid-base chemistry is involved in the American Smelting and Refining Company's (ASARCO's) sulfur dioxide capture process using aqueous dimethylaniline (Equation 2.43).

However, in this case the sulfurous acid-amine salt is heated to regenerate the much more expensive dimethylaniline solution for re-use, and obtain a concentrated sulfur dioxide gas stream. The more concentrated sulfur dioxide is now economic for acid production.

The Wellman-Lord process effectively uses the sodium sulfite/sodium bisulfite equilibrium to capture sulfur dioxide from flue gases [240, 245-247] (Equations 2.44, 2.45).

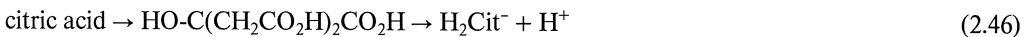
Most of the sodium bisulfite produced is converted back to sodium sulfite on regeneration, but some sodium sulfate inevitably forms from irreversible oxidation. This is crystallized out, dried, and sold as pulping chemical ("salt cake").



Absorption:



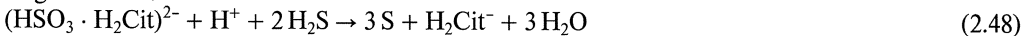
Regeneration:



Absorption:



Regeneration:



Absorption:



The citrate process, in which much development work has been invested by the U.S. Bureau of Mines and by Pfizer, Inc., uses an aqueous solution of citric acid to capture sulfur dioxide [248, 249] (Equations 2.46, 2.47).

Regeneration of the uncomplexed citric acid at the same time as formation of an elemental sulfur product from the bisulfite anion is obtained by treating the absorption solution with hydrogen sulfide [250] (Equation 2.48).

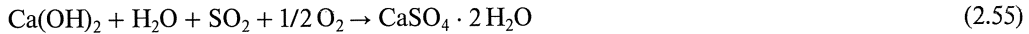
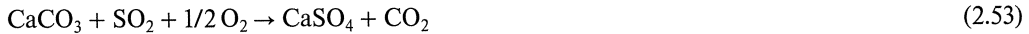
If hydrogen sulfide is not conveniently available from local process sources it may be produced on site for this requirement by reducing a part of the sulfur product of the process with methane (Equation 2.49).

The Flakt-Boliden version of the citrate process uses thermal regeneration of the citrate absorbing solution to obtain stripped citrate solution and a stream of up to 90 % sulfur dioxide at this stage [251, 252]. Recovery of a sulfur dioxide product gives flexibility to the final stage of processing as to whether liquid sulfur dioxide, sulfuric acid, or sulfur are obtained as the final product.

A further gas-liquid interaction process to a useful product is the sodium carbonate-potassium carbonate eutectic melt process, which operates at a temperature of about 425 °C, above the melting point of the eutectic [253]. Sulfur dioxide absorption takes place with loss of carbon dioxide (Equation 2.50).

The original eutectic is regenerated plus a hydrogen sulfide product obtained in a separate unit by treating the sodium sulfite with "water gas" (Equation 2.51).

Regeneration:



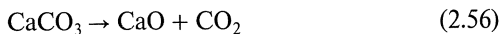
The hydrogen sulfide initial product can be subsequently converted to more useful sulfur via the Claus process. In return for the high operating temperatures required for this process, it gives a substantially dry plume, unlike the other gas-liquid interaction processes mentioned, which may be an important consideration if the process is to be operated in a fog susceptible area.

A finely powdered limestone or lime slurry in water used in a suitably designed scrubber is an effective and relatively low cost sulfur dioxide containment method [228, 245] (Equations 2.52-2.55).

With either reagent, however, a throw-away product is obtained which requires the allocation of land for lagoon disposal of spent scrubber slurries, or other systems set up to handle the waste solid [254]. A recent variation of this approach is to employ the alkalinity of flyash itself, in a water slurry, as a means of capturing sulfur dioxide [255].

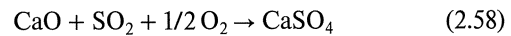
The simplest gas-solid containment systems conceptually are the direct adsorption ones. These accomplish adsorption on solids such as activated carbon, or alkalinized alumina at relatively low temperatures and ordinary pressures [256-259]. In a separate unit, when the absorbent is regenerated by heating, a more concentrated sulfur dioxide stream is produced. The more concentrated stream is now attractive as feed to an acid plant, or for liquefaction or sulfur generation.

Among the simplest systems, at least for power stations already burning powdered coal, is the use of powdered limestone injection [260]. Essentially the same burner assembly is required, and the heat of combustion of the coal is sufficient to form calcium oxide (lime) from the limestone (Equation 2.56).



The alkaline lime, in a gas-solid phase reaction, reacts with sulfur dioxide in the combustion gases to form solid particles of calcium sulfite and cal-

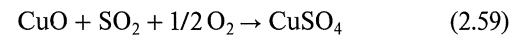
cium sulfate which are captured in electrostatic precipitators (Equations 2.57, 2.58).



The process is simple in concept, and to operate, but the gas-solid reaction is only about 20 to 60 % stoichiometrically efficient so that an excess of limestone is required for moderately efficient collection [261]. This procedure also imposes a heavier solids handling load on the precipitators, a factor which has to be considered, and it yields a throw-away product. It does, however, produce a dry plume, which may be an advantage in some situations.

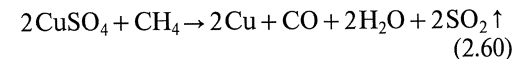
Other gas-solid containment systems, in which a significant amount of the original development work was invested by Shell, are based on copper oxide on an alumina support [262]. The absorption step of this system both oxidizes and traps the sulfur dioxide on the solid support as copper sulfate (Equation 2.59).

Uptake:

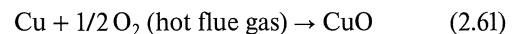


Regeneration by methane reduction is conducted in a separate unit returning sulfur dioxide, but now in more useful high concentrations (Equation 2.60).

Regeneration:



Finely divided copper on the solid support is rapidly re-oxidized to cupric oxide when it comes into contact with the hot flue gases on its return to the absorption unit (Equation 2.61).



Ferric oxide on alumina has also been tested in a very similar process [263].

A final gas-solid interaction process involves pri-

marily chemical reaction for sulfur dioxide containment. A bed of crushed coal, kept at 650 to 815 °C, is used to reduce a stream of concentrated sulfur dioxide passed through it, to elemental sulfur and carbon dioxide [264] (Equation 2.62).



2.7.5 Control of Nitrogen Oxide Emissions

Discharges of nitrogen oxides in the U.S.A. in 1981 totalled 19.5 million metric tonnes, only slightly less than the total discharges of sulfur dioxide for the same year [227]. But the transportation sector was much more significant for this classification, contributing about 8.4 million tonnes of this total. Stationary combustion sources, however, were still the most significant contributor to this classification with a total of 10.2 million tonnes, followed by industrial sources which totalled about 950 thousand tonnes.

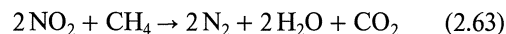
While both the primary and secondary ambient air quality standards for nitrogen oxides are somewhat higher than for sulfur dioxide the rationales behind the need for control measures are very similar, namely health effects and their influence on the pH of precipitation (Table 2.12). In addition, however, the significance of the role of nitrogen oxides in photochemical smog episodes is a further factor in the matrix of information used to set up the ambient air quality standards [265].

The mechanism of formation of nitrogen oxides (NO_x) in flue gases or combustion processes generally, is a composite of the relative concentrations of nitrogen and oxygen present and the combustion intensity (peak temperatures). Thus, small space heaters operating at lower temperatures typically produce combustion gases containing about 50 ppm NO_x , while large power plant boilers can produce flue gas concentrations of as high as 1,500 ppm [141, 266]. The formation reactions are relatively simple, involving a combination of atoms of oxygen with nitrogen and atoms of nitrogen with oxygen, both elements having finite concentrations present in atomic form at high combustion temperatures (Equations 2.20, 2.21). Because of the higher concentration of atomic species present at high temperatures rather than low, and because of the very rapid reaction rates at high temperatures, the equilibrium of these reactions is established rapidly. A small further contribution to the nitrogen oxides in exhaust gases can come from the

oxidation of nitrogen-containing organics (combined nitrogen) in the fuel.

To decrease nitrogen oxide emissions any one or a combination of measures may be used. In utility applications one of the simplest measures, which also serves to reduce average fuel combustion and hence the costs of power generation, is to take some care over the matching of combustion rate to load requirements [267]. Fuel combustion at any rate greater than the heat removal (or load requirement) tends to produce excessive boiler and flue gas temperatures and higher nitrogen dioxide concentrations.

More fundamental equipment modifications are necessary to adopt staged combustion, or larger flame volume changes as means of decreasing NO_x formation [268]. Measures using a fuel-rich combustion core the gases from which partially reduce nitrogen oxides formed near the fuel-lean walls to nitrogen are also being tested [269] (e.g. Equations 2.24-2.27, 2.63).



A second significant factor which can assist in decreasing nitrogen oxide formation is a reduction of the excess air used in combustion processes. This option requires the installation of oxygen analyzers for the continuous monitoring of the oxygen content of flue gases coupled to automatic controls or manual reset alarms, to ensure that the excess air used for combustion stays within pre-determined limits. Changing from a practice of operating with a 15 % excess of theoretical combustion air to a 2 to 3 % excess can alone serve to decrease nitrogen oxide emissions by some 60 %, and at the same time increases energy recovery efficiency [270].

Other kinds of process changes can also serve to decrease NO_x emissions by avoiding formation to a significant extent. Among these are recirculation of a fraction of the flue gas to decrease peak combustion temperatures [271], a measure which has also had some success in decreasing automotive NO_x emissions [142]. Use of pure, or enriched oxygen instead of air for combustion can also help when used with flue gas recirculation, by decreasing the concentration of nitrogen available for oxidation. Use of fuel cells for power generation could eliminate utility-originated NO_x emission, but the pure gas requirement for present fuel cell technology makes this option prohibitively expensive except in special circumstances [272].

Post-formation nitrogen oxide emission control measures include adsorption in packed beds, with which some decrease is observed [272]. But this method is not particularly effective. It is also not a very practical method either for utilities or for transportation sources. Ammonia or methane reduction of NO_x to elemental nitrogen is also an effective method, which is cost-effective for high concentration sources such as nitric acid plants [273]. Details of this procedure are discussed with nitric acid technology. Two stage scrubbing, the first stage using water alone, and the second using aqueous urea, has also been proposed as an effective post-formation NO_x control measure [274].

Relevant Bibliography

1. CRC Handbook of Environmental Control, R.G. Bond and C.P. Straub, editors, CRC Press, Cleveland, 1972, Volume 1, Air Pollution
2. Patty's Industrial Hygiene and Toxicology, G.D. Clayton and F.E. Clayton, editors, 3rd edition, Wiley, New York, 1978, Volume 1, General Principles
3. Air Pollution, 2nd edition, A.C. Stern, editor, Academic Press, New York, 1968
Volume 1. Air Pollution and Its Effects
Volume 2. Analysis, Monitoring, Surveying
Volume 3. Sources of Air Pollution and Their Control
4. Air Pollution, 3rd edition, A.C. Stern, editor, Academic Press, New York. Volume 1. Air Pollutants, Their Transformation and Transport, 1976. Also Volumes 2, and 5, 1977
5. W.L. Faith and A.A. Atkisson, Jr., Air Pollution, 2nd edition, Wiley-Interscience, New York, 1972
6. Air Pollution Abstracts, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, from volume 1, 1969
7. L.B. Lave, E.G. Seskin, and M.J. Chappie, Air Pollution and Human Health, Johns Hopkins University Press, Baltimore, 1977
8. Air Pollution and Lichens, B.W. Ferry, M.S. Baddeley and D.L. Hawkesworth, editors, Athlone Press, London, 1973
9. W.H. Smith, Air Pollution and Forests: Interactions Between Air Contaminants and Forest Ecosystems, Springer-Verlag, New York, 1981
10. Cleaning Our Environment, A Chemical Perspective, 2nd edition, American Chemical Society, Washington, 1978
11. H. Brauer and Y.B.G. Varma, Air Pollution Control Equipment, Springer-Verlag, New York, 1981

12. D.E. Painter, Air Pollution Technology, Reston Publishing Co., Reston, Virginia, 1974
13. J.M. Marchello, Control of Air Pollution Sources, Marcel Dekker, Inc., New York, 1976

References

1. E. Cook, Scientific American 225 (3), 134, Sept. 1971
2. B. Bolin, Scientific American 224 (3), 124, Sept. 1970
3. R.E. Newell, Scientific American 225 (1), 32, Jan. 1971
4. C.S. Wong, Science 200, 197, April 14, 1978
5. C.F. Cullis, Chem. In Brit. 14 (8), 384, Aug. 1978
6. C.C. Delwiche, Scientific American 224 (3), 136, Sept. 1970
7. S.J. Williamson, Fundamentals of Air Pollution, Addison-Wesley, Reading, Massachusetts, 1973
8. Air Pollution Handbook, P.L. Magill, F.R. Holden, and C. Ackley, editors, McGraw-Hill, New York, 1956
9. R. Findley, National Geographic 159 (1), 3, Jan. 1981
10. Mount St. Helens: Researchers Sort Data, Chem. Eng. News 58 (23), 19, June 9, 1980
11. Symposium to Mark 1883 Eruption of Krakatoa, Chem. Eng. News 61 (28), 138, July 11, 1983
12. A. Nohl and F. Le Guern, Chromat. Rev. 8 (2), 8, Oct. 1982
13. Mount St. Helens Stirs Chemical Interest, Chem. Eng. News 58 (34), 28, Aug. 25, 1980
14. Effects of Mercury in the Canadian Environment, M.B. Hocking and J.A. Jaworski, editors, National Research Council, Ottawa, 1979
15. W.W. Vaughn and J.H. McCarthy, Jr., U.S. Geol. Surv. Prof. Paper No. 501-D, D 128 (1964)
16. S.H. Williston, J. Geophys. Res. 73 (22), 7051, (1968)
17. F.A. Fischback, J. Envir. Health 38 (6), 382, May/June 1976
18. V.V. Kingsley, Bacteriology Primer in Air Contamination Control, University of Toronto Press, Toronto, 1967
19. T.J. Wright, V.W. Greene, and H.J. Paulus, J. Air Polln Control Assoc. 19 (5), 337, May 1969
20. E.D. King, R.A. Mill, and C.H. Lawrence, J. Envir. Health 36 (1), 50, July/Aug. 1973
21. D.C. Blanchard, Saturday Review, 60, Jan. 1, 1972
22. S.A. Berry and B.G. Notion, Water Research 10, 323 (1976)
23. Atmospheric Aerosol: Source Air/Quality Relationships, ACS Symposium Series No. 167, American Chemical Society, Washington, 1981

24. J.A. Dorsey and J.O. Burckle, *Chem. Eng. Prog.* 67(8), 92, Aug. 1971
25. Research Appliance Co., Allison Park, Pennsylvania, U.S.A.
26. Five Nights News Roundup, Canadian Broadcasting Corp., Toronto, Nov. 9, 1972
27. L. Svarovsky, *Chem. Ind. (London)*, 626, Aug. 7, 1976
28. Air Pollution, Volume III, Sources of Air Pollution and Their Control, 2nd edition, A.C. Stern, editor, Academic Press, New York, 1968
29. M.H. Chatterton and I.E. Lund, *Chem. Ind. (London)* 636, Aug. 7, 1976
30. A.W. Gnyp, S.J.W. Price, C.C. St. Pierre, and J. Steiner, *Water and Polln Control*, 111(7), 40, July 1973
31. M.J. Pilat, D.S. Ensor and J.C. Bosch, *Atmos. Envir.* 4, 671 (1970)
32. Introductory Analytical Techniques for Airborne Particulate Matter, Application Procedure AP308, Millipore Corp., Bedford, Massachusetts, 1972
33. W.G. Hyzer, *Research/Development* 26(4), 50, April 1975
34. New Sampler Separates Large, Small Samples, *Chem. Eng. News* 56(44), 23, Oct. 30, 1978
35. Detection and Analysis of Particulate Contamination, Millipore Corp., Bedford, Massachusetts, 1966
36. W.C. McCrone, R.G. Draftz, and J.G. Delly, *The Particle Atlas*, Ann Arbor Science Publishers, Ann Arbor, Michigan, 1971
37. M. Beer, R.W. Carpenter, L. Eyring, C.E. Lyman, and J.M. Thomas, *Chem. Eng. News* 59(33), 40, Aug. 17, 1981
38. K. Anlauf, L.A. Barrie, H.A. Wiebe, and P. Fellin, *Can. Research* 13(2), 49, Feb. 1980
39. R. Dams, J. Billiet, C. Block, M. Demuynck, and M. Janssens, *Atmos. Envir.* 9, 1099 (1975)
40. M.A. Kay, D.M. McKown, D.H. Gray, M.E. Eichor and J.R. Vogt, *Amer. Lab.* 5(7), 39, July 1973
41. Toxic Metals in Air, *Chem. In Can.* 25(9), 6, Oct. 1973
42. M.B. Jacobs, *The Chemical Analysis of Air Pollutants*, Interscience, New York, 1960
43. Air Pollution Vol. II, Analysis, Monitoring, and Surveying, 2nd edition, A.C. Stern, editor, Academic Press, New York, 1968
44. Analysis of Industrial Air Pollutants, Papers by P.R. Harrison, H.W. Georgii et al, MSS Information Corp., New York, 1974
45. J. Walinga and A.H.C. Hendriks, *Can. Res. Devel.* 7, 36, March/April 1974
46. Air Pollution Control Part III, Measuring and Monitoring Air Pollutants, W. Strauss, editor, Wiley-Interscience, New York, 1978
47. T.A. Rooney, *Applic. Note AN 228-6*, Hewlett Packard, Washington, 1977
48. Tenax for Trapping, *Gas-Chrom Newsletter* 21(2), 8, June 1980
49. M.B. Hocking and G.W. Lee, *Water, Air and Soil Polln* 8, 255, (1977)
50. W.J. Blaedel and V.W. Meloche, *Elementary Quantitative Analysis, Theory and Practice*, Harper and Row, New York, 1963
51. R.B. Fischer, *Quantitative Chemical Analysis*, 2nd edition, W.B. Saunders Co., Philadelphia, Pennsylvania, 1961
52. M.B. Jacobs, *The Chemical Analysis of Air Pollutants*, Interscience, New York, 1960
53. K. Leichnitz, *Detector Tube Handbook*, 3rd edition, Draegerwerk AG, Lubeck, W. Germany, 1976
54. R.M. Ash and J.R. Lynch, *J. Amer. Ind. Hygiene Assoc.* 32(8), 552, Aug. 1971
55. J. Rowland, *Varian Instr. Applic.* 15(1), 15, 1981
56. J.J. Havlena, D. Hocking, and R.D. Rowe, *The Photography of Sulfur Recovery Plant Plumes*, Proc. Alta Sulfur Gas Workshop II, Kananaskis, Alta., Jan. 16-17, 1975, page 30
57. Photographing SO₂ Emissions, *Chem. in Can.* 26(11), 16, Dec. 1974
58. Quantitative Analysis with the Miran Gas Analyzer, Wilks Scientific, South Norwalk, Connecticut, Seminar, May 1973
59. P.L. Hanst, A.S. Lefohn, and B.W. Gay, Jr., *Appl. Spectr.* 27(3), 188 (1973)
60. J. Fleming, *Chem. In Brit.* 13(9), 328, Sept. 1977
61. J. Fleming, *Chem. In Brit.* 13(10), 377, Oct. 1977
62. J.N. Pitts, Jr., B.J. Finlayson-Pitts, and A.M. Winer, *Envir. Science and Techn.* 11(6), 568, June 1977
63. E.D. Hinkley and P.L. Kelly, *Science* 171(3,972), 635, Feb. 19, 1971
64. B.L. Sharp, *Chem. In Brit.* 18(5), 342, May 1982
65. J.R. Alkins, *Anal. Chem.* 47(8), 752A, July 1975
66. J.A. Hodgeson, W.A. McClenny, and P.L. Hanst, *Science* 182, 248, Oct. 19, 1973
67. E.D. Hinkley, *Env. Science and Tech.* 11(6), 564, June 1977
68. W.F. Herget and W.D. Connor, *Env. Science and Tech.* 11(10), 962, Oct. 1977
69. Instrumental Analysis, H.H. Bauer, G.D. Christian, and J.E. O'Reilly, editors, Allyn and Bacon, Boston, 1978
70. F.W. Karasek, *Research/Development* 27(11), 42, Nov. 1976
71. M.J.E. Hewlins, *Chem. In Brit.* 12(11), 341, Nov. 1976
72. D.A. Lane and B.A. Thomson, *J. Air Polln Control Assoc.* 31, 122, Feb. 1981
73. F.W. Karasek, *Can. Research* 13(4), 30, April 1980
74. Advances in Mass Spectrometry, Volume 8B, Proc. of the 8th International Mass Spectrometry

- Conf., Oslo, 12-18 Aug., 1979, Heyden and Son, pages 1,422-1,428, and 1,480-1,489
75. Instrumentation in Analytical Chemistry, articles collected by A.J. Senzel, American Chemical Society, Washington, 1973
 76. D. Betteridge and H.E. Hallam, *Modern Analytical Methods*, The Chemical Society, London, 1972
 77. R. Perry and R.M. Harrison, *Chem. In Brit.* 12 (6), 185, June 1976
 78. ASTM Validates Air Pollution Test Methods 51, 13, March 5, 1973
 79. M.R. Midgett, *Envir. Science and Tech.* 11 (7), 655, July 1977
 80. *Industrial Hygiene and Toxicology*, 2nd edition, F.A. Patty, editor, Interscience, New York, 1963, volume II, 1963
 81. *Cleaning Our Environment, A Chemical Perspective*, 2nd edition, Committee on Environmental Improvement, American Chemical Society, Washington, 1978
 82. *California Air Environment* 4 (3), 12, spring 1974
 83. *Patty's Industrial Hygiene and Toxicology*, 3rd edition, G.D. Clayton and F.E. Clayton, editors, John Wiley and Sons, New York, 1981, volume 2A, *Toxicology*
 84. *Air Pollution Damage to Vegetation*, J.A. Naegle, editor, American Chemical Society, Washington, 1973
 85. D. Hocking and M.B. Hocking, *Envir. Polln (London)* 13, 57 (1977)
 86. A.A. Loman, *Alberta Ambient Air Quality Standards For Sulfur Dioxide, Foliar Sulfur Dioxide Symptoms on Forest Vegetation and Impact on Growth and Vigour*, in *Proceedings of Alberta Sulphur Gas Research Workshop II*, Kananaskis, Alta., Jan. 16, 1975, Queen's Printer, Edmonton, Alberta
 87. *Environmental Detectives Study Clues*, *Chemecology* 6, June 1983
 88. W. Summer, *Odour Pollution of Air*, CRC Press, Cleveland, Ohio, 1971
 89. U. Kirschaum, R. Klee, and L. Stenbing, *Staub-Reinhalt. Luft* 31 (1), 21, Jan. 1971, cited by *Air Polln Abstr.* 10586, June 1971
 90. W.C. Denison and S.M. Carpenter, *A Guide to Air Quality Monitoring with Lichens*, Lichen Technology Inc., Corvallis, Oregon, 1973
 91. O.L. Gilbert, *The Effect of SO₂ on Lichens and Bryophytes around Newcastle upon Tyne*, in *Proc. 1st European Congress on the Influence of Air Pollution on Plants and Animals*, Centre for Agric. Publishing and Documentation, Wageningen, 1969, page 223
 92. J.J. Barkman, *The Influence of Air Pollution of Bryophytes and Lichens*, in *Proc. 1st European Congress on the Influence of Air Pollution on Plants and Animals*, Centre for Agric. Publishing and Documentation, Wageningen, 1969, page 197
 93. A.C. Skorepa and D.H. Vitt, *A Quantitative Analysis of Lichen Vegetation in Relation to SO₂ Pollution at Rocky Mountain House*, in *Proceedings of Alberta Sulfur Gas Research Workshop II*, Kananaskis, Alta., Jan. 16, 17, 1975, Queen's Printer, Edmonton, Alberta
 94. A.C. Skorepa and D.H. Vitt, *A Quantitative Study of Epiphytic Lichen Vegetation in Relation to SO₂ Pollution in Western Alberta*, Information Report NOR-X-161, Northern Forest Research Centre, Edmonton, Alberta, October 1976
 95. *Lichen Chart*, *Things of Science*, Cambridge, 1972
 96. D.V. Bates, *A Citizen's Guide to Air Pollution*, McGill-Queen's University Press, Montreal, 1972
 97. *Man, Health, and Environment*, B.Q. Hafen, editor, Burgess Publishing Co., Minneapolis, Minnesota, 1972
 98. *Air Pollution*, Vol. I, *Air Pollution and Its Effects*, 2nd edition, A.C. Stern, editor, Academic Press, New York, 1968
 99. L. Hodges, *Environmental Pollution*, Holt, Rinehart, and Winston, New York, 1973
 100. J. Mage and G. Batta, *Chemie und Industrie*, 27, 1961 (1932), cited by reference 8
 101. J.A. Kerr, J.G. Calvert, and K.L. Demerjian, *Chem. In Brit.* 8 (6), 252, June 1972
 102. J.G. Calvert, *Envir. Science and Tech.* 10 (3), 248, March 1976
 103. J.N. Pitts, Jr., and B.J. Finlayson, *Angew. Chem. (Internat. Edition)* 14 (1), 1, Jan. 1975
 104. P.L. Hanst, *J. Air Polln Control Assoc.* 21 (5), 269, May 1971
 105. E. Hessvedt, *Geophys. Norvegica* 31 (2), 1 (1975)
 106. *Power Plants May Be Major Ozone Source*, *Chem. Eng. News* 52, 22, Oct. 28, 1974
 107. R.M. Harrison and C.D. Holman, *Chem. In Brit.* 18 (8), 563, Aug. 1982
 108. R.M. Harrison and C.D. Holman, *Atmos. Envir.* 13, 1,535 (1979)
 109. E.B. Cowling, *Envir. Science and Tech.* 16 (2), 110 A, Feb. 1982
 110. G.E. Likens, *Chem. Eng. News* 54 (48), 29, Nov. 22, 1976
 111. *Research Summary, Acid Rain*, M. Schaefer, editor, U.S. Environmental Protection Agency, RD-674, Washington, ca. 1980
 112. G.E. Likens, R.F. Wright, J.N. Galloway and T.J. Butler, *Scientific American* 241 (4), 43, Oct. 1979
 113. L.R. Ember, *Chem. Eng. News* 59 (37), 20, Sept. 14, 1981
 114. B. Hileman, *Envir. Science and Tech.* 15 (10), 1,119, Oct. 1981
 115. L.R. Ember, *Chem. Eng. News* 60 (47), 25, Nov. 22, 1982
 116. B. Hileman, *Envir. Science and Tech.* 17 (6), 232 A, June 1983

117. R.E. Newell, *Scientific American* 224 (1), 32, Jan. 1971
118. S.A. Changnon, Jr., *Science* 205, 402, July 27, 1979
119. T.F. Hatch, in *The Air We Breathe*, S.M. Farber, editor, C.C. Thomas, Springfield, Illinois, 1961, Cited by reference 7
120. S.K. Friedlander, *Envir. Science and Tech.* 7 (13), 1, 115, Dec. 1973
121. R.J. Seltzer, *Chem. Eng. News* 54 (44), 21, Oct. 25, 1976
122. W. Lepkowski, *Chem. Eng. News* 55 (42), 26, Oct. 17, 1977
123. B. Bolin, *Scientific American* 225 (9), 124, Sept. 1970
124. C.S. Wong, *Science* 200, 197, April 14, 1978
125. E. Aynsley, *New Scientist* 44, 66, Oct. 9, 1969
126. T.L. Brown, *Energy and the Environment*, C.E. Merrill Publishing Co., Columbus, Ohio, 1971
127. A.H. Oort, *Scientific American* 225 (9), 54, Sept. 1970
128. B.J. Palmer, *Envir. Letters* 5 (4), 249 (1973)
129. CO₂ Buildup's Effect on Climate Explored, *Chem. Eng. News* 55 (31), 18, Aug. 1, 1977
130. H. Wexler, *Scientific American* 186 (4), 74, April 1952
131. K.S. Groves, S.R. Mattingly and A.F. Tuck, *Nature* 273, 711, June 29, 1978
132. M.J. Molina and F.S. Rowland, *Nature* 249, 810 (1974)
133. Nitrogen Fertilizers May Endanger Ozone, *Chem. Eng. News* 53 (47), 6, Nov. 24, 1975
134. R.P. Turco and R.C. Whitten, *Atmos. Envir.* 9, 1, 045 (1975)
135. L.C. Glasgow, P.S. Gumerman, P. Meakin, and J.P. Jesson, *Atmos. Envir.* 12, 2, 159, (1978)
136. R.M. Baum, *Chem. Eng. News* 60 (37), 21, Sept. 13, 1982
137. Chlorofluorocarbons in the Environment: The Aerosol Controversy, T.M. Sudgen and T.F. West, editors, Society of Chemical Industry, E. Horwood Publishing, Chichester, 1980
138. R.A. Rasmussen, M.A.K. Khalil, S.A. Penkett, and N.J.D. Prosser, *Geophys. Res. Letters* 7 (10), 809, Oct. 1980
139. R.A. Rasmussen, M.A.K. Khalil, and R.W. Daluge, *Science* 211, 285, Jan. 16, 1981
140. H.S. Sandhu, *Meteorological Factors and Photochemical Air Pollutants over Edmonton, Alberta*, VIIIth International Photochemistry Conference, Edmonton, Alberta, Aug 7-13, 1975. *J. Photochem.* 5 (2), 88, March 1976
141. G.S. Parkinson, *Chem. In Brit.* 7 (6), 239, June 1971
142. G.J.K. Acres, *Chem. Ind. (London)*, 905, Nov. 16, 1974
143. J.J. Mikita and E.N. Cantwell (Dupont), *Exhaust Manifold Thermal Reactors—A Solution to the Automotive Emissions Problem*, 68th Ann. Meeting, National Petrol. Refiners Assoc., San Antonio, Texas, April 5-8, 1970
144. E.N. Cantwell, *Hydroc. Proc.* 53 (7), 94, July 1974
145. Why So Many New Cars Run So Poorly, *Consumer Reports* 37 (4), 196, April 1972
146. M.K. McAbee, *Chem. Eng. News* 53 (47), 14, Nov. 24, 1975
147. J.D. Butler, *Chem. In Brit.* 8 (6), 258, June 1972
148. Three Way Catalyst Cleans Auto Exhaust, *Chem. Eng. News* 55 (11), 26, March 14, 1977
149. H.K. Newhall, *California Air Envir.* 5 (1), 1, Fall 1974
150. Auto Emissions Control Faces New Challenges, *Chem. Eng. News* 58 (11), 36, March 17, 1980
151. G.J.K. Acres and B.J. Cooper, *Platinum Metals Review* 16 (3), 74, July 1972
152. M.E. Hilburn, *Chem. Soc. Revs.* 8 (1), 63 (1979)
153. L.R. Ember, *Chem. Eng. News* 58 (25), 28, June 23, 1980
154. P.L. Dartnell, *Chem. In Brit.* 16 (6), 308, June 1980
155. *Airborne Lead in Perspective*, National Academy of Sciences, Washington, 1972
156. *Lead in the Canadian Environment*, National Research Council, Ottawa, 1973
157. T.D. Leah, *The Production, Use, and Distribution of Lead in Canada*, Environmental Contaminants Inventory Study No. 3, Inland Waters Directorate, Burlington, Ontario, 1976
158. A.N. Manson and H.W. de Koning, *Water and Polln Control* 111 (9), 70, Sept. 1973
159. D. Turner, *Chem. In Brit.* 16 (6), 312, June 1980
160. T.J. Chow, *Nature* 225, 295 (1970)
161. N.I. Ward and R.R. Brooks, *Envir. Polln* 17, 7 (1978)
162. R.M. Harrison and D.P.H. Laxen, *Chem. In Brit.* 16 (6), 316, June 1980
163. N.I. Ward, R.R. Brooks, E. Roberts, and C.R. Boswell, *Envir. Science and Tech.* 11 (9), 917, Sept. 1977
164. New Systems Provide Useful Measurements of Auto Particulate Emissions, *Hydroc. Proc.* 49 (12), 23, Dec. 1970
165. New Particulate Trap Lowers Lead Emissions 90 %, *Hydroc. Proc.* 51 (12), 24, Dec. 1972
166. K. Habibi, *Envir. Science and Tech.* 7 (3), 223, March 1973
167. H.K. Newhall, *Calif. Air Envir.* 5 (1), 5, Fall 1974
168. J. Dunn, *Popular Science* 207 (5), 102, Nov. 1975
169. J. Daniels, *La Recherche* 11 (114), 938, Sept. 1980
170. L.R. Babcock, Jr., *J. Air Polln Control Assoc.* 20 (10), 653, Oct. 1970
171. E.G. Walther, *J. Air Polln Control Assoc.* 22 (5), 353, May 1972
172. D. Carleton-Jones and H.B. Schneider, *Chem. Eng.* 75 (10), 166, Oct. 14, 1968

173. Increased Heavy Metal Around Sudbury's Smelters, *Water and Polln Control* 111 (6), 48, June 1973
174. C.F. Barrett, *Roy. Inst. Chem. Revs.* 3 (2), 119, Oct. 1970
175. B. Bringfelt, *Atmos. Envir.* 2 (11), 575, Nov. 1968
176. E.C. Halliday, *Atmos. Envir.* 2 (9), 509, Sept. 1968
177. M. Overend, *Water and Polln Control* 110 (4), 76, April 1972
178. C. Simpson, *Eng.* 209, 578, June 5, 1970
179. E. Jeffs and A. Conway, *Eng.* 207, 796, May 30, 1969
180. Tallest Chimney in the World, *Eng.* 209, 178, Feb. 20, 1970
181. Very Tall Stacks Not Too Useful, *Chem. Eng. News* 56 (8), 23, Feb. 20, 1978
182. L.R. Ember, *Chem. Eng. News* 61 (25), 27, June 20, 1983
183. H.F. Elkin and R.A. Constable, *Hydroc. Proc.* 51 (10), 113, Oct. 1972
184. *Chemical Engineers' Handbook*, 4th edition, J.H. Perry, editor, McGraw-Hill, New York, 1963
185. A.F. Taggart, *Handbook of Mineral Dressing, Ores, and Industrial Minerals*, John Wiley and Sons, New York, 1945, page 6-1
186. Coal Agglomeration, *Chem. In Can.* 23 (11), 10, Nov. 1971
187. R.A. Meyers, *Hydroc. Proc.* 54 (6), 93, June 1975
188. H.A. Hancock and T. Betancourt, The Effect of the Addition of Chemical Oxidants on the Desulphurization of Cape Breton Coal by Ferric Sulphate Leaching, *Proc. 28th Chemical Engineering Conference, Halifax, Nova Scotia, Oct. 22-28, 1978*, plus other reports by the same authors
189. Coal and Coke Technology, *Chem. In Can.* 31 (2), 26, Feb. 1979
190. W. Worthy, *Chem. Eng. News* 53 (27), 24, July 7, 1975
191. New Way to Cope with Sulfur Oxides, *Hydroc. Proc.* 51 (9), 19, Sept. 1972
192. Clean Fuel from Coal, *Hydroc. Proc.* 51 (10), 42, Oct. 1972
193. F.K. Schweighardt and B.M. Thames, *Anal. Chem.* 50 (9), 1,381, Aug. 1978
194. Microbial Desulfurization of Coal, *Mech. Eng.* 100, 46, Dec. 1978
195. Coal Conversion: New Processes from Old, *Chem. Eng. News* 55 (36), 24, Sept. 5, 1977
196. R.L. Rawls, *Chem. Eng. News* 55 (4), 26, Jan. 24, 1977
197. R. Dagani, *Chem. Eng. News* 58 (1), 27, Jan. 7, 1980
198. Dow Details Coal Liquefaction Process, *Chem. Eng. News* 58 (27), 32, July 7, 1980
199. Coal Conversion at a Stalemate, *Chem. Eng. News* 57 (10), 18, March 5, 1979
200. C.M. McKinney, *Hydroc. Proc.* 51 (10), 117, Oct. 1972
201. C.W. Siegmund, *Hydroc. Proc.* 49 (2), 89, Feb. 1970
202. The Technology and Costs to Remove Sulfur from Oil Based Fuels, *Chem. In Can.* 23 (9), 25, Oct. 1971
203. Desulfurization Refinery Capacities, *Env. Science and Tech.* 7 (6), 494, June 1973
204. J. Yulish, *Chem. Eng.* 58, June 14, 1971
205. P. Grancher, *Hydroc. Proc.* 57 (9), 155, Sept. 1978
206. P. Grancher, *Hydroc. Proc.* 57 (9), 257, Sept. 1978
207. E.P. Mednikov, *Acoustic Coagulation and Precipitation of Aerosols*, translated by C.V. Larrick, Consultants Bureau, New York, 1965
208. Sound Pulses Clean Foul Air, *Chem. Eng.*, 52, Aug. 24, 1970
209. M.B. Hocking, *J. Envir. Systems* 5 (3), 163 (1976)
210. *Cleaning Our Environment, The Chemical Basis for Action*, American Chemical Society, Washington, 1969, page 36
211. J.N. Pitts, Jr. and B.J. Finlayson, *Angew. Chem. (Internat. Edition)* 14 (1), Jan. 1975
212. R.R. Manzone and D.W. Oakes, *Polln Eng.* 5 (10), 23, Oct. 1973
213. Airco Develops Solvent Recovery System, *Chem. Eng. News* 58 (4), 7, Jan. 28, 1980
214. G.D. Arnold, *Chem. Ind. (London)*, 902, Nov. 16, 1974
215. Fume-incineration Design Saves Fuel, *Can. Chem. Proc.* 61 (2), 31, Feb. 1977
216. D.E. Waid, *Chem. Eng. Prog.* 68 (8), 57, Aug. 1972
217. R.D. Ross, *Chem. Eng. Prog.* 68 (8), 59, Aug. 1972
218. Paint, Energy and the Environment, *Chem. In Can.* 26 (4), 24, April 1974
219. L.A. O'Neill, *Chem. Ind. (London)*, 464, June 5, 1976
220. Industry Now Leads in Paint Usage, *Can. Chem. Proc.* 63 (6), 37, June 6, 1979
221. C.M. Hansen, *Ind. Eng. Chem., Prod. Res. Dev.* 16 (3), 266, (1977)
222. New Mixes Meet Air Quality Tests, *Can. Chem. Proc.* 63 (6), June 6, 1979
223. C.A. Law, *Chem. In Can.* 30 (8), 24, Sept. 1978
224. Air Quality Rules Boost High Solids Coatings, *Chem. Eng. News* 60 (11), 5, March 15, 1982
225. J. Cross, *Chem. In Brit.* 17 (1), 24, Jan. 1981
226. Powder Coating Group Starts Up Programs, *Chem. Eng. News* 59 (36), 16, Sept. 7, 1981
227. *National Air Quality and Emissions Trends Report, 1981*, U.S. Environmental Protection Agency, 450/4-83-011, Research Triangle Park, North Carolina, 1983
228. N.Kaplan and M.A. Maxwell, *Chem. Eng.* 84, 127, Oct. 17, 1977
229. W.W. Kellogg, R.D. Cadle, E.R. Allen, A.L. Lazarus, and E.A. Martell, *Science* 175 (4,402), 587, Feb. 11, 1972

230. J.A. Garland, D.H.F. Atkins, C.J. Readings, and S.J. Caughey, *Atmos. Envir.* 8, 75 (1974)
231. D.D. Davis, The Photochemistry and Kinetics of Power Plant Plumes, VIIIth Photochem. Conf., Edmonton, Alberta, Aug. 7-13, 1975. *J. Photochem.* 5 (2), 88, March 1976
232. M.A. Lulis and C.R. Phillips, *Atmos. Envir.* 11, 239 (1977)
233. W.H. White, *Envir. Science and Tech.* 11 (10), 995, Oct. 1977
234. M.A. Hughes, *Chem. Ind. (London)*, 1,042, Dec. 20, 1975
235. P.J. Bailes, C. Hanson, and M.A. Hughes, *Chem. Eng.* 83, 86, Aug. 30, 1976
236. M.C. Kuhn, *Mining Eng.* 29 (2), 79, Feb. 1977
237. R. Derry, *Chem. Ind. (London)*, 222, March 19, 1977
238. P. Grancher, *Hydroc. Proc.* 57 (9), 155, Sept. 1978
239. P. Grancher, *Hydroc. Proc.* 57 (9), 257, Sept. 1978
240. New Units Aimed at Fluegas Clean-up, *Chem. In Can.* 62 (7), 26, July 1978
241. Hydrogen Sulphide Removal by the Stretford Liquid Purification Process, *Chem. Ind. (London)*, 883, May 19, 1962
242. A.A. Siddiqi and J.W. Tenini, *Hydroc. Proc.* 56 (10), 104, Oct. 1977
243. Stop Air Pollution and Recover Sulphur, *Proc. Eng.*, 9, Sept. 1976
244. P. Bonnifay, R. Dutriau, S. Frankowiak, and A. Deschamps, *Chem. Eng. Prog.* 68 (8), 51, Aug. 1972
245. New Scrubbers Tackle SO₂ Emissions Problem, *Chem. Eng. News* 56 (45), 24, 1978
246. System Removes SO₂ From Stack Gas, *Chem. Eng. News* 55 (45), 35, Nov. 7, 1977
247. B.H. Potter and T.L. Craig, *Chem. Eng. Prog.* 68 (8), 53, Aug. 1972
248. Citric Acid Used in SO₂ Recovery, *Chem. Eng. News* 49 (24), 31, June 14, 1971
249. Pfizer to Test Citric Acid For Converting SO₂ into Sulfur, *Chemecology*, 7, Dec. 1972
250. F.S. Chalmers, *Hydroc. Proc.* 53 (4), 75, April 1974
251. S. Bengston, *Chem. In Can.* 33 (1), 24 (+ cover), Jan. 1981
252. Flue Gas Desulfurization to be Tested, *Chem. Eng. News* 57 (14), 20, April 2, 1979
253. SO₂ Removal, *Chem. Eng. News* 49 (6), 52, Feb. 8, 1971
254. Flue Gas Scrubbing With a Limestone Slurry, *Can. Chem. Proc.* 59 (10), 8, Oct. 1975
255. Flyash Replaces Limestone in Sulfur Dioxide Removal, *Chem. Eng. News* 57 (32), 26, Aug. 6, 1979
256. G.N. Brown, S.L. Torrence, A.J. Repik, J.L. Stryker, and F.J. Ball, *Chem. Eng. Prog.* 68 (8), 55, Aug. 1972
257. S.L. Torrence, U.S. Patent 3,667,908, June 6, 1972, to Westvaco Corp. Cited by *Air Polln Abstr.* 5 (1), 69, Jan. 1974
258. J.E. Newell, *Chem. Eng. Prog.* 65 (8), 62, Aug. 1969
259. J.H. Russell, J.I. Paige, and D.L. Paulson, Evaluation of Some Solid Oxides as Sorbents of Sulfur Dioxide, U.S. Bureau of Mines, RI 7,582, Washington, 1971
260. H.L. Falkenberry and A.V. Slack, *Chem. Eng. Prog.* 65 (12), 61, Dec. 1969
261. T.H. Chilton, *Chem. Eng. Prog.* 67 (5), 69, May 1971
262. F.M. Dautzenberg, J.E. Nader, and A.J.J. Ginneken, *Chem. Eng. Prog.* 67 (8), 86, Aug. 1971
263. Reduction of Low Concentrations of SO₂ by CO, *Can. Chem. Proc.* 55 (7), 49, July 1971
264. Coal Converts Sulfur Dioxide to Sulfur, *Design News* 34, 18, Nov. 20, 1978
265. J.N. Pitts, Jr. and B.J. Finlayson, *Angew. Chem. (Internat. Edition)* 14 (1), 1, Jan. 1975
266. D.R. Bartz, *Calif. Air Envir.* 5 (1), 10, Fall 1974
267. R.B. Rosenburg, *Eng. Digest* 17 (7), 27, Aug. 20, 1971
268. R. Rawls, *Chem. Eng. News* 59 (13), 19, March 30, 1981
269. Low NO_x Burner to be Demonstrated in Utah, *Chem. Eng. News* 59 (17), 16, April 27, 1981
270. A.M. Woodward, *Hydroc. Proc.* 53 (7), 106, July 1974
271. NO_x Yield Reduced by New Design, *Can. Chem. Proc.* 63 (2), 30, Feb. 5, 1979
272. Zeroing in on Flue Gas NO_x, *Envir. Science and Tech.* 3 (9), 808, March 1969
273. R.A. Searles, *Platinum Metals Rev.* 17 (2), 57, April 1973
274. Two Processes to Control Emissions of Nitrogen Oxides, *Can. Chem. Proc.* 59 (11), 4, Nov. 1975
275. D.J. Spedding, *Air Pollution*, Clarendon Press, Oxford, 1974
276. Joint Air Pollution Study of St. Clair-Detroit River Areas For International Joint Commission, Canada and the United States, International Joint Commission, Ottawa and Washington, 1971
277. Matheson-Kitagawa Toxic Gas Detector System, Matheson, Lyndhurst, N.J., July 1980
278. Gastec Precision Gas Detector System, Gastec Corp., Tokyo, ca. 1974
279. The Clean Air Act, Annual Report 1977-78, Ottawa, cited by M. Webb, The Canadian Environment, W.B. Saunders Co., Can. Ltd., Toronto, 1980
280. *Industrial Hygiene and Toxicology*, 2nd edition, Volume I, General Principles, F.A. Patty, editor, Interscience, New York, 1958
281. Ottawa Sets Timetable for Cleanup, *Can. Chem. Proc.* 58 (3), 19, March 1974

282. C.G. Cortelyou, Chem. Eng. Prog. 65(9), 69, Sept. 1969
283. A.V. Slack, Envir. Science and Tech. 7(2), 110, Feb. 1973
284. R.L. Andrews, Combustion (New York) 49(19), Oct. 20, 1977
285. R.B. Engdahl and H.S. Rosenberg, Chemtech. 8(2), 118, Feb. 1978
286. Air Pollution, L.C. McCabe, editor, McGraw-Hill Book Co., New York, 1952. Cited by reference 8