

# MEASUREMENT TOOLS FOR POLLUTION SOURCES AND AMBIENT CONCENTRATIONS

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## Summary

Chemical techniques have been applied for the detection of airborne pollutants, before the relative recent surge of interest in the chemistry of the atmosphere. However, with the recognition of the severity of many of the so-called London smog episodes and the identification in the 1940s of photochemical smog came the need to monitor a whole host of primary and secondary pollutants. We go through some common techniques for detecting and measuring gas phase pollutants at a given point or over relative short periods. The bases of the monitoring techniques, their advantages and disadvantages, and the gaseous pollutants that have been successfully monitored in ambient air by these methods are emphasized. The concentration is on the major criteria and non-criteria pollutants and on the methods to measure their concentrations, which either have been successfully used in ambient air studies or show promise and are at the field testing stage.

### 1. Introduction

Chemical techniques have been applied for the detection of airborne pollutants, before the relative recent surge of interest in the chemistry in the atmosphere. A good example is nitric acid. Nitric acid in the air was inferred in the 1800s by its reaction with calcium carbonate. However, with the recognition of the severity of many of the so-called London smog episodes and the identification in the 1940s of photochemical smog came the need to monitor a whole host of primary and secondary pollutants. We will go through some common techniques for detecting and measuring gas phase pollutants at a given point or over relative short pathlengths. The bases of the monitoring techniques, their advantages and disadvantages, and the gaseous pollutants that have been successfully monitored in ambient air by these methods are emphasized. The concentration will be on the major criteria and non-criteria pollutants and on the methods to measure their concentrations, which either have been successfully used in ambient air studies or are promising and at the field of testing stage.

Detecting the various species, to establish their presence in the atmosphere, is an important first step. However measuring them, and quantitatively determining their concentrations, is essential for the elucidation of the relative importance of various reactions in the atmosphere. This will be essential in formulating cost-effective control strategies. It is important to notice that detection and measurement do not always go together.

One of the first obvious manifestations of photochemical air pollution was the effect on rubber products that rapidly hardened and cracked. This phenomenon was used as a

means of monitoring the major recognized second pollutants, photochemical oxidants, which cause this effect. In the 1950s the oxidants in the ambient air were monitored by measuring the time for cracking to appear in a piece of rubber placed in ambient air. This time was inversely proportional to ozone (O<sub>3</sub>) concentration and by comparison to the effects of laboratory produced O<sub>3</sub>. An estimate of the oxidant concentration could be made subsequently. Several wet chemical techniques for monitoring photochemical oxidants were developed. The most widespread technique used was the potassium iodide (KI) method. The basis of this method is the oxidation of the colorless iodide ion into brown I<sub>2</sub>.



The formation of I<sub>2</sub> was monitored colorimetrically or by coulometry. The O<sub>3</sub> efficiently oxidizes the I<sup>-</sup> in solution but some other air pollutants can also contribute to the I<sup>-</sup>→I<sub>2</sub> conversion. For example NO<sub>2</sub> and PAN (peroxyacetyl nitrate) react in a manner similar to O<sub>3</sub>, although with lesser efficiencies. So, bubbling air in an iodide solution gives a reading of total oxidant, which includes a combination of various pollutants such as O<sub>3</sub>, NO<sub>2</sub> and PAN. Beside the pollutants that give a positive response, some interfere negatively, such as SO<sub>2</sub>, which gives 100% negative response and must be removed from the air prior to analysis.

The KI wet chemical technique is not specific for one pollutant, and in fact the term oxidant is defined by the technique itself: That is, oxidant in any species that is giving a positive response in the KI method. This technique of measuring and reporting total oxidants was used almost exclusively until the mid 1970s. However, data were obtained suggesting that this technique was not accurate and reliable as had been previously accepted. Data obtained with the KI method gave a distorted view of the geographical oxidant distribution. Today, the Ultraviolet method is most commonly used to monitor O<sub>3</sub> in ambient air and is accepted as an equivalent method by US Environmental Protection Agency.

The determination of the geographical distribution of a gas phase air pollutant in the ambient air not only has socioeconomic implications but impacts control strategy options as well. One way of developing such control strategy options is the use of air quality models. A basic step in the use of such models that mathematically describe the emissions, meteorology and chemistry in the air basin is the validation against existing ambient air data. The model is used to predict pollutant concentrations for various days for which monitoring data exist. Then, adjustments are made in the model to optimize agreement between the observed and predicted pollutant concentrations. The impact of various control strategy options on air quality is then predicted using the model. It is clear that the impacts of the resulting control strategy options cannot be more reliably predicted than the accuracy of the model itself allows for. This is critically dependent on the ambient air data against which is validated.

It is of great importance that the methods of measurement of air pollutants are accurate, sensitive, and specific. Only physical techniques satisfy these requirements and these techniques have undergone substantial development over the last few years. Even then,

there remain a number of important pollutants for which no sufficient sensitive physical monitoring technique yet exists.

## 2. The Air Pollution System

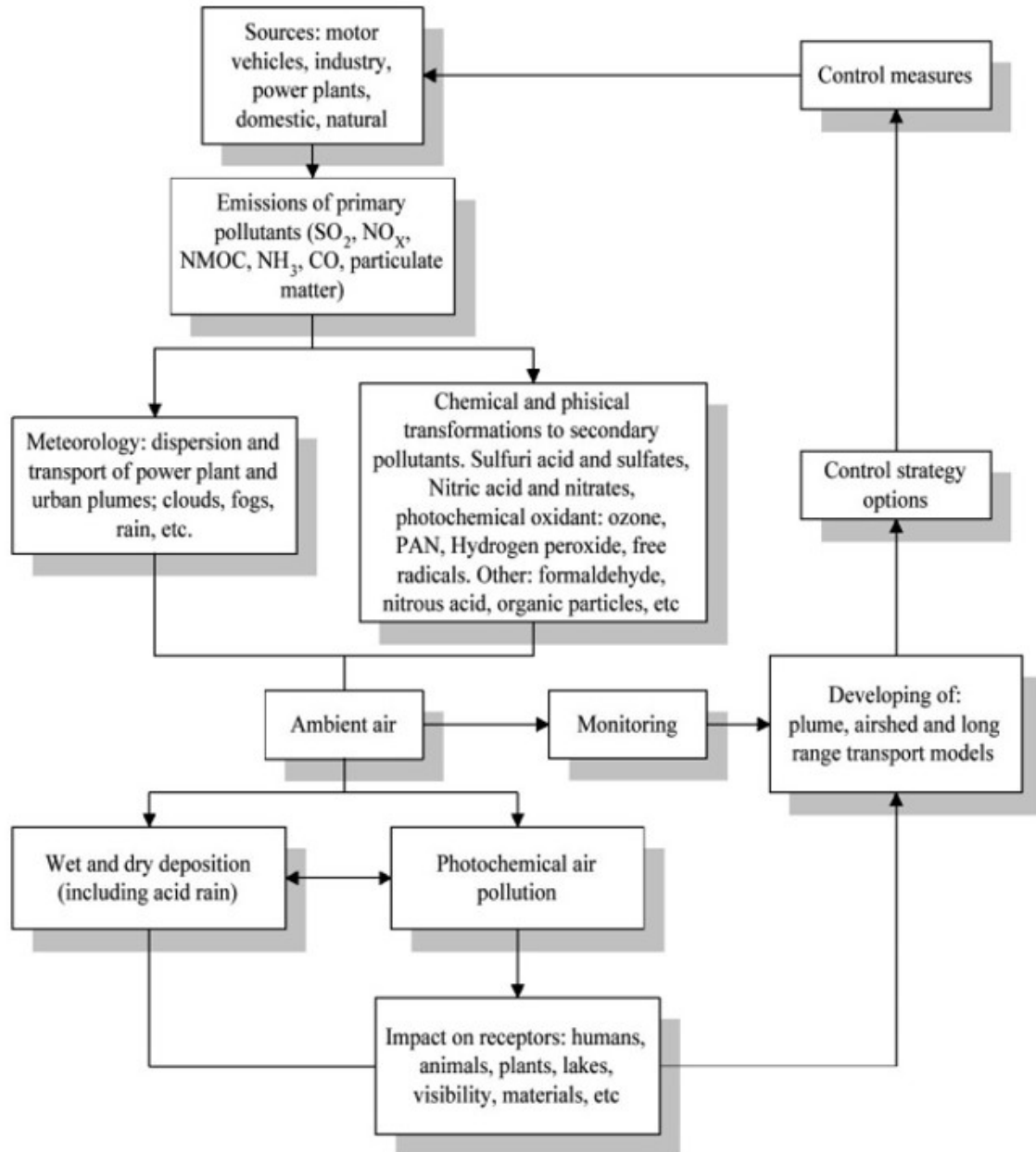


Figure 1. Air pollution system.

The air pollution system (Figure 1) starts with the various sources of anthropogenic and natural emissions (e.g. volcanoes) in the atmosphere. They are divided into primary and secondary pollutants. Primary pollutants are emissions that have a direct polluting effect in their original form, and they are emitted directly into the air from their sources. The secondary pollutants are those formed in the atmosphere as a result of chemical reactions among themselves, or between wastes and the atmosphere. An example is ozone, a component of photochemical smog. It is a secondary pollutant formed from the

reaction between sunlight and nitrogen oxides and/or hydrocarbons, both of which are themselves primary pollutants.

Primary pollutants from human activities include:

- oxides of sulfur, nitrogen, carbon and related compounds;
- organic compounds such as hydrocarbons (fuel vapor and solvents);
- acid gases including sulfuric acid and hydrochloric acid;
- particulate matter such as smoke and dust;
- metal oxides and related compounds including those of lead, cadmium, copper and iron;
- fluorides;
- toxic and non-toxic odors;
- radioactive substances.

Secondary pollutants include nitrogen dioxide, ozone and other components of photochemical smog.

In the atmosphere, the pollutants are subjected to dispersion and transportation and simultaneously to chemical and physical transformations. The pollutants may be removed at the earth's surface via wet or dry deposition and can *impact* a variety of receptors such as humans, animals, aquatic ecosystems, etc. From detailed knowledge of the emissions, topography, meteorology and chemistry, mathematical models can be developed that predict the concentrations of primary and secondary pollutants as a function of time at various locations. These models are validated by comparing their predictions with the observed concentrations of the pollutants measured in appropriate ambient air monitoring programs. The validated models are then used in combination with the documented impacts on receptors to develop various control strategy options.

A number of pollutants have been documented to have effects on people, plants or materials at concentrations found in the ambient air. The US Environmental Protection Agency (EPA) has set, in 1990, National Ambient Air Quality Standards for pollutants considered harmful for public health and the environment. EPA has set two types of air quality standards:

- **Primary standards** set limits to protect public health, including the health of 'sensitive' populations such as asthmatics, children, and the elderly.
- **Secondary standards** set limits to protect public welfare, including protection against decreased visibility, damage to animals, crops, vegetation, and buildings.

The EPA Office of Air Quality Planning and Standards (OAQPS) has set National Ambient Air Quality Standards for seven principal pollutants, which are called 'criteria' pollutants. Table 1 lists these compounds and their approximate ranges of concentrations observed from remote areas to severe air pollution episodes in urban areas. Table 2 gives the National Ambient Air Quality Standards set by EPA. Units of measurement for the standards are parts per million (ppm) by volume, milligrams per cubic meter of air ( $\text{mg}/\text{m}^3$ ), and micrograms per cubic meter of air at 25 °C ( $\mu\text{g}/\text{m}^3$ ). Ambient air standards have two components: a concentration and a time. For example,

for O<sub>3</sub> it is 0.12 ppm for 1 hour; this means that to avoid deleterious effects the O<sub>3</sub> concentration should not exceed 0.12 ppm for more than 1 hour.

Criteria Pollutant	Typical range of concentrations
CO	<0.2-50 ppm
SO <sub>2</sub>	<1 ppb-2ppb
O <sub>3</sub>	0.01-0.5 ppm
NO <sub>2</sub>	<1 ppb-0.5 ppm
NMHC*	<65 ppbC-1.5 ppmC
Total suspended particules	5-1500 µg m <sup>-3</sup>
Lead	0.0001-10 µg m <sup>-3</sup>

\* Non Methane Hydrocarbons

Table 1. Criteria pollutants and approximate ranges of concentrations observed from remote areas to severe air pollution episodes in urban areas.

	Primary		Secondary	
	Time	Concentration	Time	Concentration
<b>Carbon Monoxide (CO)</b>	8-hour Average	9 ppm (10 mg/m <sup>3</sup> )		
	1-hour Average	35 ppm (40 mg/m <sup>3</sup> )		
<b>Nitrogen Dioxide (NO<sub>2</sub>)</b>	Annual Arithmetic Mean	0.053 ppm (100 µg/m <sup>3</sup> )	Annual Arithmetic Mean	0.053 ppm (100 µg/m <sup>3</sup> )
<b>Ozone (O<sub>3</sub>)</b>	1-hour Average	0.12 ppm (235 µg/m <sup>3</sup> )	1-hour Average	0.12 ppm (235 µg/m <sup>3</sup> )
	8-hour Average	0.08 ppm (157 µg/m <sup>3</sup> )	8-hour Average	0.08 ppm (157 µg/m <sup>3</sup> )
<b>Lead (Pb)</b>	Quarterly Average	1.5 µg/m <sup>3</sup>	Quarterly Average	1.5 µg/m <sup>3</sup>
<b>Particulate &lt; 10 µm (PM-10)</b>	Annual Arithmetic Mean	50 µg/m <sup>3</sup>	Annual Arithmetic Mean	50 µg/m <sup>3</sup>
	24-hour Average	150 µg/m <sup>3</sup>	24-hour Average	150 µg/m <sup>3</sup>
<b>Particulate &lt; 2.5 µm (PM-2.5)</b>	Annual Arithmetic Mean	15 µg/m <sup>3</sup>	Annual Arithmetic Mean	15 µg/m <sup>3</sup>
	24-hour Average	65 µg/m <sup>3</sup>	24-hour Average	65 µg/m <sup>3</sup>
<b>Sulfur Dioxide (SO<sub>2</sub>)</b>	Annual Arithmetic Mean	0.03 ppm (80 µg/m <sup>3</sup> )	3-hour Average	0.50 ppm (1300 µg/m <sup>3</sup> )
	24-hour Average	0.14 ppm (365 µg/m <sup>3</sup> )		

Table 2. US national ambient air quality standards

### 3. Spectroscopic Monitoring Techniques

Spectroscopic monitoring techniques are physical techniques that are based on the interaction of electromagnetic radiation (light) with the atoms and molecules of interest. Molecules and atoms can emit (emission spectrometry) or absorb (absorption spectrometry) electromagnetic radiation in characteristic frequencies, which can be used

to identify them. Concentrations of atoms or molecules can be determined by the intensity of the emitted or absorbed light. Spectroscopic monitoring techniques is accurate, sensitive, and specific, and, for these reasons, have undergone substantial development over the last few years.

### 3.1. Emission Spectrometry

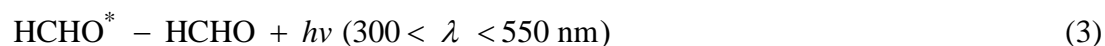
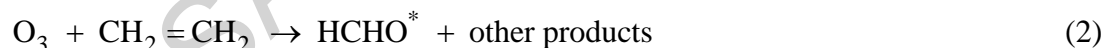
By emission spectrometry techniques the molecules are excited to a higher electronic state, and the intensity of the emitted radiation as it returns to the ground state is monitored. Electronically excited species can be produced chemically (chemiluminescence), by absorption of light (fluorescence) or by introducing the substance of interest into a flame (flame photometry).

#### 3.1.1. Chemiluminescence

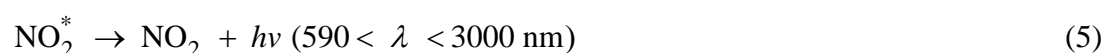
Chemiluminescence is the production of light from the energy released in a chemical reaction and is used to monitor a variety of pollutants, including O<sub>3</sub> and NO. A number of chemical reactions generate products not in their lower energy state, but in their upper levels. The energy released from the reaction is channeled internally into electronic (E), vibrational (V) or rotational energy of one or more of the products, rather than being released as heat. The excited product molecules may emit this energy as light.

By the chemiluminescence technique, air containing the pollutant to be measured is drawn into the monitoring instrument where it is mixed with a species with which it reacts to produce light. The emission is proportional to the pollutant concentration. In the case of O<sub>3</sub> two reactions are used:

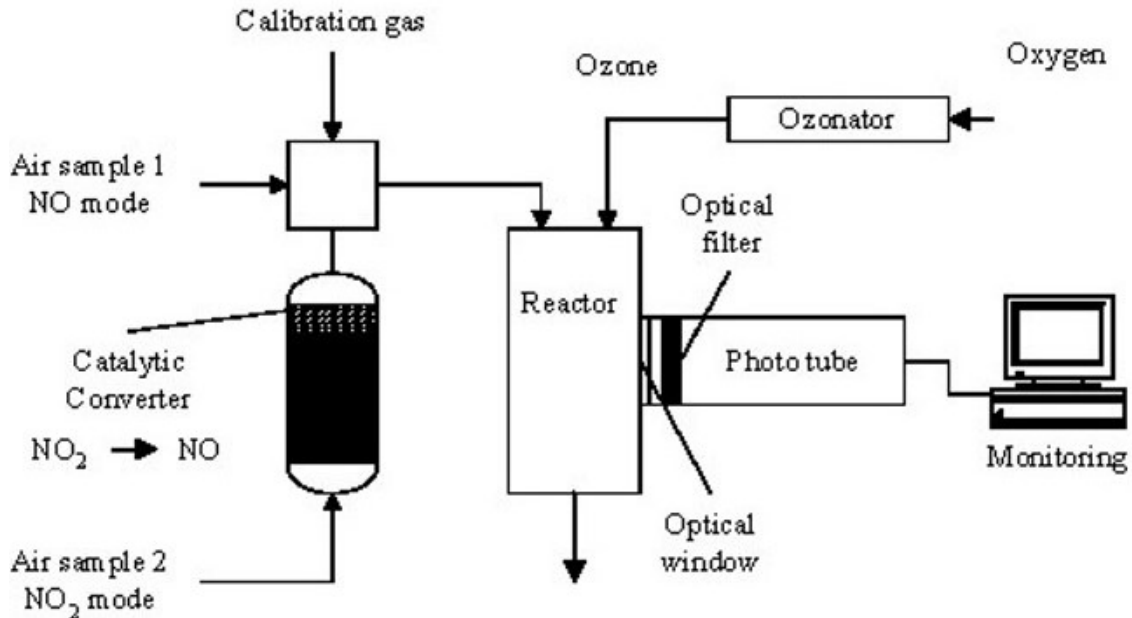
1. Reaction with ethylene (CH<sub>2</sub>=CH<sub>2</sub>), where electronically excited formaldehyde (HCHO\*) is produced which is the light emitting species. At low pressures all simple olefins emit light upon reaction with O<sub>3</sub>. The emitting species have been identified as electronically excited formaldehyde and in some cases, dicarbonyl compounds and vibrationally excited OH in its ground state. At atmospheric pressure in commercial instruments based on ozone (O<sub>3</sub>) - ethylene (CH<sub>2</sub>=CH<sub>2</sub>) reactions all emissions, except that of due to HCHO, are effectively quenched.



2. Reaction with nitric oxide (NO) where electronically excited nitrogen dioxide (NO<sub>2</sub>\*) is produced, which is the emitting species.



The nitric oxide is also monitored using reactions (4) and (5) where excess O<sub>3</sub> is used. Also converting them first to NO, several other important gaseous nitrogen containing pollutants can be monitored. A good example is the conversion of nitrogen dioxide to NO thermally with molybdenum at 200 °C or chemically using FeSO<sub>4</sub>.



$$\text{NO}_2 \text{ concentration} = \text{NO measured from air sample 2} - \text{NO measured from air sample 1}$$

Figure 2. Chemiluminescence nitric oxide analyzer.

In commercial NO<sub>x</sub> analyzers the instrument switches automatically between the NO (direct injection) mode and the NO<sub>x</sub> (passing the air-stream over a converter) mode (Figure 2). The difference between the two is the total NO<sub>x</sub> minus NO, which is often mainly NO<sub>2</sub>.

It is clear that any compounds in the air other than NO<sub>x</sub> that will be converted to NO in the converter will interfere with the measurement of NO<sub>x</sub>. Gaseous nitrogenous species, such as PAN (peroxyacetyl nitrate), organic nitrates, NH<sub>3</sub>, HNO<sub>3</sub>, N<sub>2</sub>O<sub>5</sub>, ClNO<sub>x</sub>, and HONO, are measured since these are also reduced to NO.

Ammonia (NH<sub>3</sub>), for example, can interfere in the NO<sub>x</sub> measurement, when the converters' operating temperature is about 600 °C since it is oxidized to NO on a variety of metallic surfaces. Ammonia is generally not a problem when chemical converters are used which operate at temperatures as low as 200 °C.

Nitric oxide (HNO<sub>3</sub>) can be measured by the chemiluminescence method using a nylon filter, which removes quantitatively the HNO<sub>3</sub> from the air sample. The HNO<sub>3</sub> concentration is determined by the difference between the NO<sub>x</sub>/NO concentration with and without the nylon filter in the incoming air stream. The HONO may act as interference in the HNO<sub>3</sub> measurements by this technique since it is also removed



quantitatively by the nylon filter. Since HONO rapidly photolyzes during the day, it is more likely to present a problem at night when significant HONO concentrations may accumulate.

Chemiluminescence techniques are more specific than wet chemical techniques (e.g. KI method) because of the relatively few reactions that give off light. In addition, filters or monochromators can be used to isolate the wavelengths of interest in order to discriminate against interfering emissions. However, in the NO<sub>x</sub> measurement some selectivity is lost in the NO<sub>x</sub> reduction because of the number of compounds that can be reduced to NO and hence give positive responses.

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#### Biographical Sketches

**Christopher J. Koroneos:** studied Chemical Engineering in Columbia University where he also earned his Doctorate. His research interests are in the areas of Environmental Engineering, Energy engineering, Process Engineering, Environmental process synthesis, and Life Cycle Analysis. At the present time he is a Special Scientist and Visiting Professor at the Laboratory of Heat Transfer and Environmental Engineering of the Mechanical Engineering Department of Aristotle University of Thessaloniki, in Greece. His professional experience includes being Professor at the Department of Chemical Engineering at Columbia University and head of Program Development of Earth Engineering Center at Columbia University. He has many years experience in the industry working as Senior Research Engineer, Process Engineer, Process Development Engineer and Consultant. He has multiple professional affiliations and many professional awards.

**Nicolas Moussiopoulos,** Director of LHTEE: studied Mechanical Engineering in Karlsruhe, Germany, Ph.D. in Thermodynamics 1982. 1982-1989 – leading a Research Group at the University of Karlsruhe. February 1989 appointed Professor and Director of the Laboratory of Heat Transfer and Environmental Engineering at the Aristotle University Thessaloniki, Greece. Honorary Professor of the University of Karlsruhe since 1996. Coordinator of EUROTRAC projects and member of the Application Project, and the Scientific Steering Committee of EUROTRAC-2. His research work deals primarily with the development and application of atmospheric wind and dispersion models. He participated actively at more than 20 international research projects, and has more than 200 scientific publications, including 8 books and about 30 papers in peer-reviewed journals. 1990 he received the Heinrich Hertz Award.

**George D. Roubas** is a graduate from Chemical Engineering Department (1992-1997) of Polytechnic School of the Aristotle University of Thessaloniki (AUT). His research interests are in the areas of Fluid

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