

EMISSION SAMPLING AND ANALYSIS

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Summary

After a brief survey of emission parameters, conventions, units, potential errors and quality assurance, the sampling of gases and their gas chromatographic separation, detection and quantification are discussed in this chapter. Other analytical methods, with emphasis on electro-optical monitoring are discussed in *Effluent Gas Monitoring*,

particulate sampling, monitoring and characteristics in *Dust-Particle Formation and Characteristics*.

1. Survey

1.1. Characteristics to be analyzed

Gaseous effluents, such as flue gases and off-gases, must be monitored carefully in order to control:

- Plant operation,
- Emission of pollutants, and sometimes both.

Either oxygen or carbon dioxide are always monitored, in order to verify combustion conditions, more in particular the excess of combustion air, a factor important in determining the thermal efficiency of boiler plant and the quality of combustion. Also the dust and the moisture content in the off-gas may provide important indications on the quality of raw materials and plant operation.

A second factor requiring general attention is the quality of combustion, addressed in *Pollution Control through Efficient Combustion Technology*. This quality can be ascertained from a few parameters, such as CO, C_xH_y, TOC.

Finally, there are the numerous pollutants, the control of some of which is addressed in *Control of Gaseous Emissions*. Pollutants may be measured on the basis of numerous and sometimes specific process or raw materials related factors. Frequently covered are the values for dust, CO, SO₂, NO_x, C_xH_y, TOC, HCl (incinerators). Rarely measured are SO₃, Cl₂, N₂O.

The nature and limit values of these parameters, and the method and frequency of their determination are given in both general codes and specific conditions, stipulated in the operating permits. Detailed procedures vary from country to country, although EU-Directives and Federal Codes may decide on minimum requirements and also on measures to be taken (notification, even halting plant operation) in case limit values are being exceeded for a specified time period.

Generally, different procedures are required to measure immission values. The latter are typically five or six orders of magnitude lower than the corresponding emission values.

Immission values normally are not related to a single plant, but much more - to atmospheric conditions, such as stability and wind velocity, which determine the vertical mixing and advection of pollutants in the atmosphere.

Still, authorities may decide on general measures, such as informing sensitive groups in the population, limiting traffic, forced switching to a cleaner fuel, etc.

General Properties

The following parameters will almost always be measured in the gas, for nearly all types of industrial installations:

- The dust concentration (mg m^{-3}).
- The main combustion-related compounds are H_2O , O_2 and CO_2 (vol. %). The major, inert component, N_2 , is implicitly derived by difference. A 'real' nitrogen analysis is only possible by gas chromatography of the gas, using a thermal conductivity detector and hydrogen or helium as a carrier gas.
- The main pollutants (mg m^{-3}): typically CO , SO_2 , NO , NO_2 , C_xH_y , generally expressed as TOC, HCl (incinerators). Rarely measured are SO_3 , Cl_2 , N_2O .

Inorganic and mineral compounds

The major inorganic and mineral compounds are:

- Sulfur oxides (SO_2 , SO_3),
- Nitrogen oxides (NO , NO_2), and, still seldom, N_2O ,
- Halogen compounds (chlorides and fluorides), HCl (in incinerators), salts (from fumes, and wet scrubbers, that neutralize the gases) and sometimes even Cl_2 (the latter is formed from HCl in the presence of a catalyst),
- Heavy and volatile metals such as mercury, cadmium, thallium, arsenic, lead, zinc, copper. In contrast to the former parameters these are related mainly to residual dust and aerosols. Sometimes a distinction is made between metals arrested on a filter of specified pore size, typically between 0.5 and 2 μm .

Organic compounds

The major organic compounds of interest are:

- Total Organic Carbon (TOC), a sum parameter of organics in a gas stream, as detected by a Flame Ionization Detector (FID), without further identification of the compounds involved. The latter are evaluated by comparison with a calibration gas, generally propane, methane, or pentane. Their identity can be determined, where required, by sampling on absorbent tubes, followed by thermal desorption or solvent extraction and gas chromatographic separation, coupled with mass spectrometry.
- Specific volatile organic compounds (VOCs), such as benzene, toluene, arenes, alkanes, alkenes (popular names are: aromatics, paraffins, olefins), and a number of solvents, some of which are chlorinated,
- Polycyclic Aromatic Hydrocarbons (PAH), typically the Borneff group, or the 15 EPA PAHs.
- Polychlorinated biphenyls (PCB), a group of 209 different biphenyls, substituted once to ten times by chlorine.
- PCDD/PCDF, i.e. Polychlorinated Dibenzo-p-dioxins and Polychlorinated Dibenzofurans, generally abridged together to 'Dioxins', a group of 75 different dibenzo-p-dioxins and 135 different dibenzofurans, substituted once to eight times by chlorine. Routinely, only the tetra- to octachlorinated congeners are considered, with emphasis on those with a planar structure, and characterised by

a 2,3,7,8-substitution pattern.

1.2. Concentration Units

Two different systems are actually used to express gas phase concentrations, the first one on a volume/volume (which is also a mol/mol) basis and the second one on a mass/volume ratio. The systems are mutually convertible, with conversion factors depending on the molecular weights of the compounds considered.

Volumetric units (volume/volume) are widely used for comparing the concentration of a particular gas compound to the total gas (or air) concentration. Since one mole of an ideal gas has a constant and well-known volume (22.414 liters at standard conditions, i.e. atmospheric pressure, 0° C) gaseous concentrations are usually expressed as a simple volumetric ratio, e.g.

- for common gases, in vol. % (a ratio of 1: 10²),
- for trace gases, in volume-to-volume parts per million or ppm (a ratio of 1: 10⁶), in parts per billion or ppb (a ratio of 1: 10⁹), or more seldom parts per trillion ppt (a ratio of 1: 10¹²), parts per quadrillion ppq (a ratio of 1: 10¹⁵), etc.

Sometimes ppm is written vppm, emphasizing that volume units are used, an unnecessary precaution, however, when dealing with gases.

Mass concentrations are universally used when addressing solid and liquid compounds, with as most usual unit:

$$1 \text{ mg m}^{-3} = 1,000 \text{ } \mu\text{g m}^{-3} = 1,000,000 \text{ ng m}^{-3} = 1,000,000,000 \text{ pg m}^{-3} = \dots \quad (1)$$

Emission values of standard pollutants are generally expressed in mg m⁻³, immission values in μg m⁻³. In few cases (e.g. dioxins, and other micropollutants) very low units are used, namely ng m⁻³ as order of magnitude of dioxin emissions from the sources of concern and fg m⁻³ for expressing atmospheric concentrations of dioxins. Conversion between different mass (or other) units is based on the conventional multiplier collected in the following Table 1.

Factor	Name	Symbol
10 ²⁴	Yocto-	Y
10 ²¹	Zepto-	Z
10 ¹⁸	Exa-	E
10 ¹⁵	Peta-	P
10 ¹²	Tera-	T
10 ⁹	Giga-	G
10 ⁶	Mega-	M
10 ³	Kilo-	k
10 ²	Hecto-	h
10	Deca-	da
10 ⁻¹	Deci-	d
10 ⁻²	Centi-	c

10^{-3}	Milli-	m
10^{-6}	Micro-	μ
10^{-9}	Nano-	n
10^{-12}	Pico-	p
10^{-15}	Femto-	f
10^{-18}	Atto-	a
10^{-21}	Zetta-	z
10^{-24}	Yotta-	y

[Source: <http://physics.nist.gov/cuu/Units/prefixes.html>, The NIST Reference on Constants, Units, and Uncertainty, International System of Units, SI Prefixes]

Table 1: Prefixes used with SI units

The density of a gas at standard conditions, i.e. at a temperature of 273.15° K (0° C) and a pressure of 1 atmosphere (1013 mbar), is derived from its Molecular Weight (*MW*) and standard volume. Thus, the density of carbon dioxide amounts to:

$$44.01 \text{ (g mol}^{-1}\text{)} / 22.414 \text{ (liter mol}^{-1}\text{)} = 1.964 \text{ g liter}^{-1} \quad (2)$$

to be compared with 1.293 g liter⁻¹ for air.

Converting volumetric to mass units or vice versa is relatively straightforward and proceeds by use of the relation, relating the density of gases at standard temperature and pressure as:

$$C \text{ (g Nm}^{-3}\text{)} = MW \text{ (molecular weight, in g mol}^{-1}\text{)} / 0.022414 \text{ (Nm}^3 \text{ mol}^{-1}\text{)} \quad (3)$$

According to the gas laws a rise in temperature or a decrease in pressure reduces the gas density, proportionally to the extent of the thermal expansion of the gas. Conversely, cooling and compression both enhance gas density, and hence concentrations expressed in g m⁻³.

Since it is impractical in codes, calculations, or balances to handle variable values for a gas concentration, while the relative proportions of its compounds remain unchanged, it is customary to relate concentrations to normal conditions throughout the plant. Since gas volume varies with both temperature and pressure, it is convenient to refer to this gas at standard conditions. Thus 1 m³ at standard conditions is noted Nm³ (in German literature m³_n).

1.3. Presentation of Analytical Results

Normal conditions

Analytical skills are different from those of plant operators, or of emission regulating and controlling Agencies. A series of conventions concerning the ways in which measurement results are to be expressed and reported in a uniform and standard way are necessary for allowing a ready comparison with emission norms for industrial plant, as described in National Codes and for ensuring that there are no misunderstandings.

All concentrations are expressed in relation to a unit volume of gas under normalized standard conditions (Nm^3), i.e. at a temperature of 273.15°K (0°C) and a pressure of one atmosphere (1013mbar).

Dry Basis

Codes often specify that the gas should be considered on an artificial, dry basis rather than on a real, moist one. Gases hence are normally expressed on a **dry gas basis**, so that all reported results are to be recalculated after ignoring this moisture content. This also implies that the volumetric percentage of humidity has to be experimentally determined, e.g. by cooling the gas and condensing and weighing the condensate.

Oxygen correction

When comparing emissions from different installations it is necessary to avoid internal distortions because of a variable usage of combustion or of dilution air. Hence, for emission control purposes, the concentration data are compared after their correction to a fixed value for the concentration of oxygen and moisture.

This convention avoids variability, induced by differences in humidity of air or flue gas, or by a process-related dilution of gases. Both measures have the same purpose: to avoid an artificial lowering of emission concentration values, by diluting the off-gas to be monitored with either additional air or water vapor.

For municipal solid waste incinerators, a standard concentration of 11 % O_2 and no moisture was arbitrarily selected in the well-known TA-Luft (Technische Anleitung zur Reinhaltung der Luft), one of the oldest existing Codes. The resulting corrections are often quite important, since

- Some old and small incinerators, without heat recovery, cool the flue gas by admixture of air, hence operating at a very high oxygen level (17 to 19 vol. %) in the stack gas, so that adaptation leads to ‘corrected’ results often four to five times as much as the actual ones,
- A very modern plant, for the sake of combustion control, thermal efficiency, and for minimizing the flow of gas to be cleaned operates at low oxygen values (typically 6 to 9 vol. %) in the stack gas, so that the computed concentration is lower than the actual one.

The TA-Luft standard concentration of 11 % O_2 was arbitrarily selected. Hence, other Codes may specify other concentrations, or rather be based on CO_2 concentration to standardize emission values.

In practice the raw, real results must then be recalculated by the following procedure:

- 1) first subtract all contained moisture from the gas (this subtraction inflates the resulting concentrations, in the same ratio for all pollutants),
- 2) then effect a fictitious addition or subtraction of air, to adjust the real oxygen concentration to its standard value. In practice the following formula is used:

$$C_{\text{stand.}} = C (21 - O_{2,\text{stand.}}) / (21 - O_2) \quad (4)$$

Where

$C_{\text{stand.}}$, $O_{2,\text{stand.}}$ = standardized concentration

C , O_2 = real concentration

and $O_{2,\text{stand.}}$, O_2 expressed in Vol. %, $C_{\text{stand.}}$, C in any consistent system of units.

The cited value of 11 % O_2 is atypical for gas or oil firing, since these require much less excess of air. Conversely, a number of metallurgical processes on the one hand use oxygen-enriched air, and on the other - aspire for much dilution air, leading to the practical impossibility of using this method of recalculation.

In other words, there is no logical basis for selecting a particular level of oxygen for correction, since every process has its own optimal operating conditions, and a corresponding ideal level of oxygen.

1.4. Quality of Analyses

Quality Assurance

Since analyses are very important in ensuring environmental compliance extreme care must be taken to avoid systematic and reduce random error, by procedures of quality assurance, periodic calibration, round robin testing, checking mass balances, and other common sense methods of data evaluation.

Although analytical work usually proceeds with great care there are an almost infinite number of potential interferences, chemical and physical factors that may create errors. It is essential to be aware of such possible errors, before interpreting any analytical values.

Evaluation of results

Accuracy measures the agreement between the experimental result and the true value.

Precision is the degree of agreement among a series of measurements of the same quantity and addresses the reproducibility of results rather than their correctness. Errors may be either systematic or random.

Systematic errors cause the results to vary from the correct value in a predictable manner and can often be identified and corrected. An example of a systematic error is improper calibration of an instrument.

Random errors are the small fluctuations introduced in nearly all analyses. These errors can be minimized but not eliminated. They can be treated, however, using statistical methods.

In most cases, two values are reported for quantitative analyses. The first is an estimate of the correct value for the analyzed quality, and the second indicates the random error in the analysis. Most scientists report the mean or average of the results of the laboratory assays. In specific cases, however, it is better to report the median (central value when the results are arranged in order of size), the mode (the value obtained most often) or the geometric average (the n th root of the product of all values obtained).

Statistics is used to estimate the random error that occurs during each step of an analysis, and, upon completion of the analysis, the estimates for the individual steps can be combined to obtain an estimate of the total experimental error. The most frequently reported error estimate is the standard deviation of the results; however, other values, such as **variance**, **range**, **average deviation**, or **confidence limits** at a specified probability level are sometimes reported. For the relatively small number of replicate samples that are used during chemical assays, the standard deviation (s) is calculated by using the equation where Σ represents summation, x_i represents each of the individual analytical results, a is the average of the results, and N is the number of replicate assays:

$$s = \left(\frac{\sum (x_i - a)^2}{N - 1} \right)^{1/2} \quad (5)$$

The **standard deviation** is a popular estimate of the error in an analysis because it has statistical significance whenever the results are normally distributed, i.e. errors are random. Most analytical results exhibit **normal or Gaussian behavior**, following the characteristic bell-shaped curve.

If the results are normally distributed, 68.3 percent of the results can be expected to fall within the range of plus or minus one standard deviation about the mean, as a result of random error. The units of standard deviation are identical to those of individual analytical results.

The **variance** (V) is the square of the standard deviation and is useful because it is additive throughout the several steps of the chemical analysis or indeed, any procedure. Consequently, an estimate of the total random error in the analysis can be obtained by adding the variances for each of the individual steps in the analysis.

The standard deviation for the overall analysis can then be calculated by taking the square root of the sum of the variances.

A simple measure of variability is the **range**, given as the difference between the largest and the smallest results. It has no statistical significance, however, for small data sets. Another statistical term, the **average deviation**, is calculated by adding the differences, while ignoring the sign, between each result and the average of all the results, and then dividing the sum by the number of results.

Confidence limits at a given probability level are values greater than and less than the average, between which the results are statistically expected to fall a given percentage of the time.

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Biographical Sketches

Alfons Buekens was born in Aalst, Belgium; he obtained his M.Sc. (1964) and his Ph.D (1967) at Ghent University (RUG) and received the K.V.I.V.-Award (1965), the Robert De Keyser Award (Belgian Shell Co., 1968), the Körber Foundation Award (1988) and the Coca Cola Foundation Award (1989). Dr. Buekens was full professor at the Vrije Universiteit Brussel (VUB), since 2002 emeritus. He lectured in Ankara, Cochabamba, Delft, Essen, Sofia, Surabaya, and was in 2002 and 2003 Invited Professor at the Tohoku University of Sendai.

Since 1976 he acted as an Environmental Consultant for the European Union, for UNIDO and WHO and as an Advisor to Forschungszentrum Karlsruhe, T.N.O. and VITO. For 25 years, he advised the major

industrial Belgian Bank and conducted more than 600 audits of enterprise.

Main activities are in thermal and catalytic processes, waste management, and flue gas cleaning, with emphasis on heavy metals, dioxins, and other semi-volatiles. He coordinated diverse national and international research projects (Acronyms Cycleplast, Upcycle, and Minidip). Dr. Buekens is author of one book, edited several books and a Technical Encyclopedia and authored more than 90 scientific publications in refereed journals and more than 150 presentations at international congresses. He is a member of Editorial Boards for different journals and book series.

He played a role in the foundation of the Flemish Waste Management Authority O.V.A.M., of a hazardous waste enterprise INDAVER, and the Environmental Protection Agency B.I.M./I.B.G.E. He was principal ministerial advisor in Brussels for matters regarding Environment, Housing, and Classified Enterprise (1989). Since 1970 he has been a Member of the Board of the Belgian Consumer Association and of Conseur, grouping more than a million members in Belgium, Italy, Portugal, and Spain.

He is licensed expert for conducting Environmental Impact Assessments (Air, Water, Soil) and Safety Studies regarding large accidents (Seveso Directive).

Kathleen Schroyens has studied Industrial Engineer in Chemistry (1998) at the KAHO – Ghent.

Since 1999 she is working as scientific collaborator at the Chemical Engineering department of the Vrije Universiteit Brussel. She is collaborating in projects for the European Union (MINIDIP, Haloclean) and The Flemish Government, AMINAL, preparing an inventory of all waste or product streams, derived from thermal processes that are contaminated with dioxins, performing (succinct) risk analysis and devising the measures required in order to monitor and control such streams'. She is also a collaborator in smaller assignments concerning dioxins emissions of MSWI and other industrial plants.

Johan Versieren has studied Agricultural Engineering at the University Ghent (1982) and performed additional studies and a specialisation on environment, 1987 – 1989, at the Institute “Universitaire Instelling”, Antwerpen. He has been responsible, during the last 13 years, for the air monitoring section of the laboratory SGS-Ecocare Belgium. He started in 1998 his own Environmental Laboratory specialised in air pollution monitoring, as well as emissions and immissions.

Since 1990 he is licensed in Vlaanderen for Environmental Impact Assessments (sections air, water and soil). He is also licensed for Environmental Coordinator.