

VOC MONITORING ON STATIONARY SOURCES: FROM ENVIRONMENTAL POLICIES TO TECHNICAL SOLUTIONS



In the past, the primary origin of local air pollution has been emissions from **stationary sources**. These sites include power generating plants, oil refineries, chemical plants, steel factories, cement and glass manufacturing companies, space heating, and many other industries. Pollutants are emitted into the air from these plants through **fossil fuel combustion**, **chemical processes**, and the **grinding or pulverizing of metals** for cement, fertilizers, etc.



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In USA the **Clean Air Act** was established in 1970: a comprehensive federal law that regulates air emissions from stationary and mobile sources. Under the Clean Air Act, **EPA** sets limits on certain air pollutants, including setting limits on how much can be in the air anywhere in the United States. The Clean Air Act also gives EPA the authority to **limit emissions** of air pollutants coming from sources like chemical plants, utilities, and steel mills. Individual states or tribes may have stronger air pollution laws, but they may not have weaker pollution limits than those set by EPA. The Clean Air Act requires EPA to create a list of the important categories of stationary sources of air pollution, and to establish Federal standards of performance for new sources within these categories. These **New Source Performance Standards (NSPS)** apply to newly constructed sources or those that undergo major upgrades or modifications. The standards include both equipment specifications as well as operation and measurement requirements and are published within the **EPA 40 CFR part 60**.

Directive 2010/75/EU of the European Parliament and the Council on industrial emissions (the Industrial Emissions Directive or **IED**) is the main EU instrument regulating pollutant emissions from industrial installations and was adopted on 24 November 2010. It is based on a Commission proposal recasting 7 previously existing directives following an extensive review of the policy. The IED aims to achieve a **high level of protection of human health** and the environment taken as a whole by reducing harmful industrial emissions across the EU, in particular through better application of Best Available Techniques (**BAT**). A major analytical challenge presented by stack gases is that they are often aggressive matrices, comprising both high- and low-concentration organic vapours with acidic gases, high levels of particulates, high humidity and a wide range of inorganic gases. In addition, environmental regulations require emissions of organic vapours to be maintained below defined limits, which necessitates ongoing monitoring. Methods therefore need to be reliable and able to cope with a wide range of environmental conditions, innovative analytical solutions and instrumentation will be a great help in achieving this task.

In the US, **whole-air collection methods**, such as glass 'bombs' canisters and sampling bags, are widely used for monitoring stack emissions, in accordance with (for example) **US EPA Methods 0030, 325 and 5041A**. However, these methods are limited in terms of their analyte range and real-time monitoring. Alternatively, continuous emission monitoring systems (**CEMS**) have been used as a tool to monitor the effluent gas streams resulting from combustion in industrial processes, and also as a means to comply with air emission standards. CEMS typically consist of **analyzers** to **measure gas concentrations** within the stream, equipment to **direct a sample** of that gas stream to the analyzers if they are remote, equipment to **condition the sample** gas by removing water and



other components that could interfere with the reading, **pneumatic plumbing** with valves that can be controlled by a PLC to route the sample gas to and away from the analyzers, a **calibration and maintenance system** that allows for the injection of calibration gases into the sample line, and a Data Acquisition and Handling System (**DAHS**) that collects and stores each data point and can perform necessary calculations required to get total mass emissions. The types of gases being measured and the calculations required are dependent upon the source type and each source type has its own subpart under **US EPA 40 CFR part 60 and part 75**.

Volatile organic compounds (**VOC**) are a specific class of pollutants that contain **carbon** and **hydrogen** and are characterized by their **volatility** (ability to evaporate) under standard conditions i.e. normal room temperature and pressure. VOCs are emitted to the atmosphere from a number of sources, some occurring naturally. The main contributors however are **industrial processes that use solvents**, (for example; printing, spray painting, coil coating, wood treatment etc.), **inefficient combustion** from road traffic engines and **evaporation from landfill sites**. The **U.S. EPA** regulates VOCs at Federal level in **40 CFR 59**, which is the National Volatile Organic Compound Emission Standards For Consumer And Commercial Products. VOC controls for products are typically based on the application of products, such as: **Aerosol Coatings - Architectural Coatings - Automobile Refinish Coatings - Consumer Products**.

CEN standard reference methods for total VOC measurement are:

(a) **EN 12619** of January 2013: Stationary source emissions - Determination of the mass concentration of total gaseous organic carbon - Continuous flame ionisation detector method. This European Standard specifies a **flame ionisation detector (FID)** method. It is intended for use as a standard reference method for the measurement of the mass concentration of gaseous and vaporous organic substances (expressed as TVOC) in **stationary source emissions** (e.g. emissions from waste incinerators and solvent using processes, emission measurements according to 2010/75/EU) in the concentration range up to 1 000 mg/m³. The method measures VOCs including methane, and involves extraction of a gas sample through a **heated line** to avoid condensation losses into the FID detector and other problems. The FID is **calibrated with propane** and gives a direct reading as parts per million per volume (ppm) propane equivalent of VOCs, which can be converted to a mass concentration.

b) **ISO 13199:2012**: Stationary source emissions — Determination of TVOCs in **waste gases from non-combustion processes** — **Non-dispersive infrared analyser** equipped with catalytic



converter. This standard specifies the principle, the essential performance criteria and quality assurance/quality control (QA/QC) procedures of an automatic method for measuring total TVOCs content in waste gases of stationary sources, using a NDIR analyser equipped with a catalytic converter which oxidizes VOCs to carbon dioxide. This method is suitable for the measurement of TVOCs emissions from non-combustion processes. It allows for continuous monitoring with permanently installed measurement systems, as well as intermittent measurements of TVOCs emissions. That method has been tested in the field operation for painting and printing processes, where TVOCs concentrations in the waste gases ranged from about 70 mg/m³ to 600 mg/m³.



Sampling and measurement of VOCs can generally be done in three different ways depending on the information required and the legislation in place, these are:

- a) Periodic measurements (portable)
- b) Continuous emissions monitoring (CEMs)
- c) Screening (leak detection)

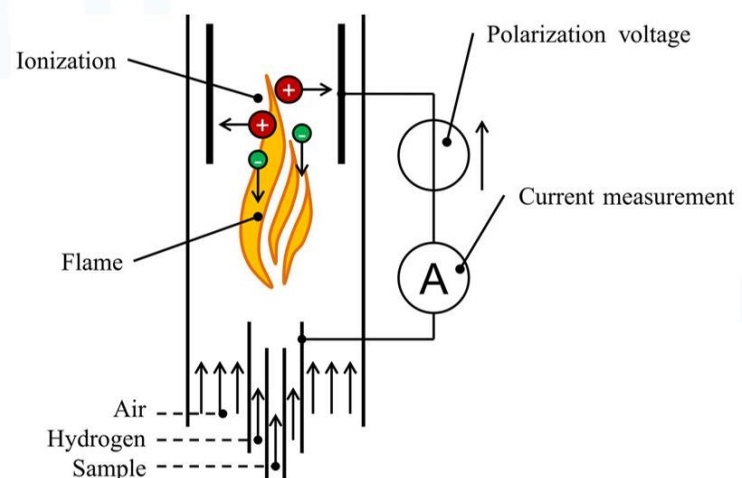


It is imperative that the sample taken when performing the periodic and continuous monitoring techniques is **representative of the overall VOC** Detection process emissions. The usual location for a representative sampling port is just prior to the VOCs exiting the process / factory boundary, in most cases via an exhaust stack, to enable measurement of emissions to atmosphere. For many **CEMs calibration** will be performed **in conjunction with a periodic type VOC analyser**.

VOC monitoring can be performed for reasons other than regulatory compliance. It can be used to **monitor the working environment**, ensuring process operators are working in a safe environment, to monitor the **performance of abatement equipment** e.g. thermal oxidisers or gas scrubbers, or as a design tool for specifying the aforementioned abatement equipment prior to purchase. In this instance, it is imperative that **long term representative sampling is carried out** to best understand the high and low concentrations of the VOCs emitted to atmosphere by the process. In many cases the abatement equipment will be designed to cope with a short-term maximum VOC output as opposed to an overall average. **Portable devices** that are easy to carry and to periodically install at the sampling point are the best candidates for these types of application.

Safety is always paramount when working with VOC monitoring equipment. Gas sampling is often done several metres high when working on exhaust stacks and care should be taken – permanent platforms (built to the correct standard) are ideal to work from, however, scaffold structures are more than adequate assuming they have also been constructed to the required standard.

Flame ionization detector (**FID**) is the most sensitive device for VOC monitoring in **combustion processes** and it is the only certified method accepted by **EN12619** and **EPA Method 25A**. Organic carbon compounds are relatively easily ionizable in a hydrogen flame, FID techniques work consequently by a gas being passed into a measurement chamber, which uses a **flame to create ions** from the VOCs. More specifically, FID analysers make use of the chemi-ionization of **organically bound carbon atoms** in a hydrogen flame to provide measurements. The measurement cell contains a pair of **electrodes**; a current is applied between them. If ions are present in the cell, the current can pass between the electrodes. The **ionization current** measured by the FID depends





upon the number of carbon-hydrogen bonds of the organic compounds burning in the fuel gas flame and the ability with which these compounds ionize. As the abundance of ions within the cell depends on the concentration of the gas, FID provides a means of measuring the concentrations of VOCs. The absolute measuring sensitivity depends on the type of fuel gas, the material of the combustion nozzle, and the detector geometry. FID does not differentiate between different gases since it responds to carbon bonds rather than to specific compounds. Thus, the result is given as total organic carbon (**TOC**). The response, however, depends on the bond type of the respective carbon atom. This means that high amounts of compounds with low FID response, for example alcohols or ethers, will lead to underestimated measurement results if they cannot be corrected with corresponding response factors. One additional problem is that the FID signal is sensitive to the oxygen content, which usually leads to a decrease of the response function (This effect is often termed **oxygen synergism**). The oxygen interference on the FID signal depends on the details of the **FID design** and operating conditions: the operating pressure, the fuel flow rate, the amount of diluent in the fuel (hydrogen) flow. The errors introduced because of oxygen synergism are significantly reduced by the use of a fuel gas consisting of a **helium/hydrogen mixture** (typically 60/40 mix), and this is almost universally used in the traditional instruments. The operating range of the FID, however, can be enhanced significantly by the use of **pure hydrogen as the fuel gas**, so this would be the preferred solution. Finally, **humidity** might also affect the analysis, so this has to be taken into account and the **FID geometry** developed properly in order to minimize this **interference**.

Using the **Polaris FID** analyser produced by **Pollution Analytical Equipment** it is possible to carry out the **VOCs monitoring according to EN 12619** without lifting accessories and heavy weights typically involved with FID analyser. So far, the portability of such analyser was a feature of FID designed for fugitive emissions from valves, flanges, gaskets, pumps or compressors monitoring. On the other hand, when VOCs are measured in chimneys according to EN 12619, the analyser must be much more robust and **fully heated to 180°C** leading to increase in size and weight. With Polaris FID analyser certified for EN 12619 the **portability** is not compromised anymore, and **miniaturization** of the flame ionization detector and volumetric sampling system results in outstanding energy savings allowing the use of **built-in rechargeable batteries** and special hydrogen storage cartridge. Since just Hydrogen is required to fuel the flame, it was possible to equip Polaris FID with a **compact bullet-proof hydrogen storage cartridge** (that use an innovative solid metal hydride technology of AB5-type alloys). This cartridge is integrated into the instrument and self-desorbs the hydrogen fuel to the flame detector at appropriate pressure and flow. Furthermore, as hydrogen is chemically bonded to a special metal alloy inside the cartridge, there is **no risk of leakage and explosion**:



hydrogen cylinder will not be a concern anymore and supply hydrogen for 30 hours for continuous analysis. The overall equipment is **resistant to high temperatures and humidity** to cope with typical situation in the stack emission. Polaris FID uses a **heated volumetric sampling system** in order to eliminate all possible cold spots and contamination ensuring the best analytical results.

In conclusion, the Polaris FID incorporates in just 13 kg and in a compact body everything needed for measuring campaign, making the best choice for the operators who have to climb chimneys of industrial settlements easily and safely.