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ENVIRONMENTAL MONITORING

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Abstract: *Environmental monitoring is a system of surveillance, forecasting, warning and intervention, which takes into account the systematic evaluation of the dynamics of qualitative characteristics of environmental factors in order to know the state of quality and their ecological significance, evolution and social implications of changes followed by appropriate measures. Monitoring involves the permits holder to make monitoring of process conditions, process releases, environmental levels and reporting the results to the regulatory authority in accordance with laws, regulation or permits.*
Keywords: *monitoring, emissions, measurement*

1. INTRODUCTION

Systematic surveillance of the variations of a certain chemical or physical characteristic of any: emission, discharge, process parameter etc. is based on repeated measurements in accordance with fixed procedures, to provide information that can lead to better decision-making about an industrial operation.
Useful for:

- Operator's:
- optimising a process;
- auditing;
- quality control;
- occupational health and safety.
- Authorities:
- compliance checking;
- environmental reporting;
- assessing charges;
- quantifying the performance of BATs.

2. CONTENT

2.1.Objectives

Monitoring programmers cover:

- Controlled emissions of waste gas and airborne particulate to air via chimney stacks;
- Controlled discharges of waste water via sewers to and from effluent treatment plants;
- Controlled disposal of solid waste to landfill sites, controlled discharges of waste water via sewers to and from effluent treatment plants;
- Controlled disposal of solid waste to landfill sites;
- Controlled disposal of solid and liquid wastes, including organic, to incinerators;
- Process raw material inputs (e.g. trace contaminants and operating conditions (e.g. process temperature, pressure and flow rate);
- Fugitive releases to air, water and land; being those that are not coming from a defined point but rather from a number of widespread points;
- Energy efficiency and water consumption;
- Noise and odor nuisances;
- In addition, receiving environments (e.g. ambient air, grass, oil surface and ground waters) may be monitored.

Emission Sources

Identification of the suitable priority level of monitoring of different releases taking into account:

- the nature, scale of the operation and variations in the process and emissions;

- resources available for monitoring.
- quantification of the total emission and not measure only some individual points very accurately or only the big point sources;
- importance of exceptional emissions (disturbance and accidental situations, such as start up and shutdowns).

Parameter Value:

- Directly measured;
- Indirectly measured by using surrogate parameters;
- Calculated by emission factors, extrapolation of other values, etc.

Monitoring Technique

Depend on the use of:

- Fixed (in-situ or on line) continuous reading instruments;
- Portable discontinuous reading instruments;
- Laboratory analysis of samples taken by fixed, in-situ, on-line time or flow proportional samplers;
- Laboratory analysis of spot samples;
- Calculations based on surrogate measurements of flow rates, raw material, contaminants, temperature, pressure etc.

Monitoring technique phases:

- Preparation;
- Generation;
- Evaluation.

Preparation

Setting up a measurement strategy, determining:

- Which objectives;
- Frequencies (risk-based approach);
- Process conditions;
- Duration;
- Measurements protocols (tools, standards procedures).
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- Duration;
- Measurements protocols (tools, standards procedures).

Generation

Depends on the:

- Information needed and specific situation;
- Direct (difficult, inaccurate or excessive costly) or indirect (process deep knowledge) measurement;
- Calculation, estimation or extrapolation.

Evaluation

Calculation of the concentration accounting:

- Operating conditions of the stream (temperature, pressure, etc.);
- Statistical treatment to reduce the amount of data;
- Interpretation in the light of the objectives.

2.2. DATA PRODUCTION CHAIN

Factors affecting the monitoring:

- Flow/amount measurement;
- Sampling;
- Sample pre-treatment;
- Sample treatment;
- Sample analysis;
- Data processing;
- Reporting.

Flow/Amount Measurement

Flow measurement accuracy has a major impact on the total load emission results:

- For waste gas flow the error can hardly be less than 5%, normal errors of 10% are often found;
- For waste water discharge an error of 5% has been recommended to be;
- For determination of the amount of solid waste, including sludge is usually made by multiplying the density and volume of the containers.

Sampling

Sampling must be representative in the time and also in space.

The sample to the laboratory should represent all that it has been discharge during, for example, a day of work (time representativeness); or if a material is being monitored, the portion of sample should represent the thousands of tones that are being introduced in the plant (space representativeness).

The sampling should carried out with no change in the composition of the sample. There are parameters in a sample that should be determined or somehow preserved, in situ as their value may change with the time.

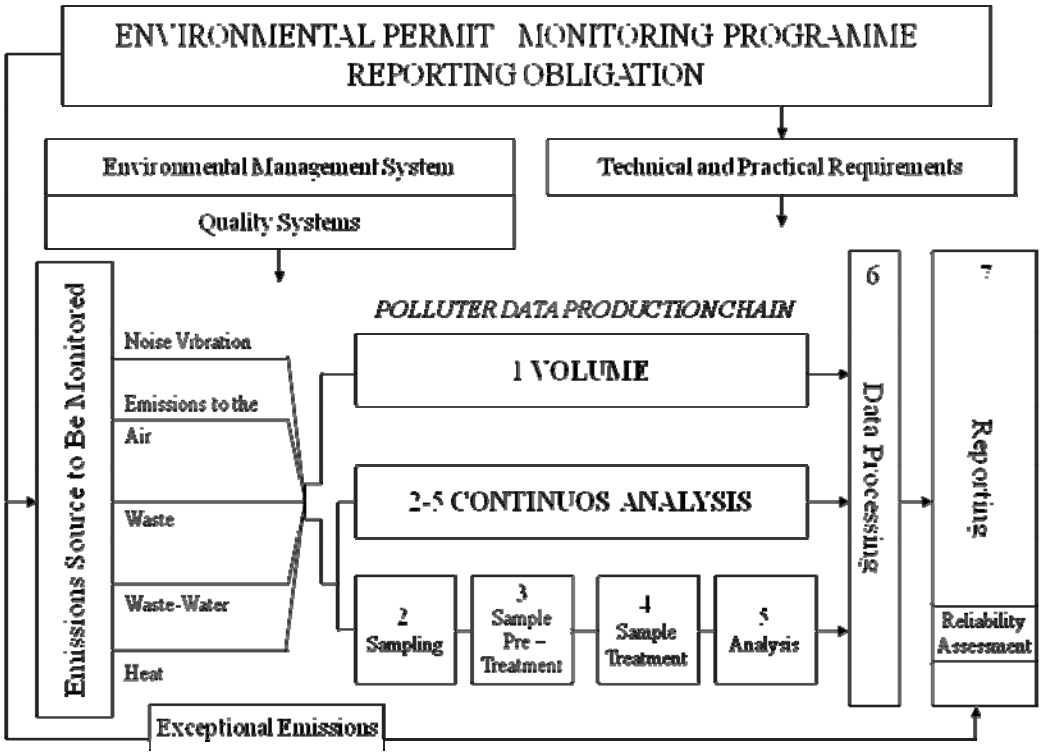

Fig. 1. Monitoring programme

The complexity is increased as the sample:

- May range from a few grams up to thousands of tones;
- May include substances that can vary widely in their nature;
- Is homogeneous or heterogeneous;
- Can be solid, gaseous or liquid.

Factors to be indicated:

- The location should be such that:
  - material is well mixed;
  - same defined points;
  - flow can be measured or known;
  - not difficult to reach;
  - no personnel risk regarding safety hazards (care of inhaling, contacting toxic substances or receiving hot discharges).
- The frequency is decided on a risk basis taking into account:
  - variability of the flow;
  - composition of the flow;
  - magnitude of the variability with respect to limit;
  - unacceptable values.
- The sampling method and/or equipment:
  - **The type of sampling**:
    - automatic time;
    - flow proportional;
    - manual spot.
  - The **size** of individual samples and bulking arrangements to provide composite samples;
  - The type of sample e.g. sample for single or multiple determinant analysis;
  - The personnel in charge of taking the samples should be skilled.
- Label attached to the sample:
  - All previous characteristics;
  - A unique sample identification number assigned from a sequentially number register;
  - Date and time of sampling;
  - Sample preservation;
  - Process relevant details;

- References to measurements made at the time when the sample is taken.

Sample Pre-treatment

- To preserve the value of the parameters, while storage and transporting of the sample:
  - keeping the sample at a suitable temperature (typically at 4ºC);
  - adding certain chemicals to fix the composition.
- Pre-treatment of the sample must be carried out according to the analysing programme.
- Clearly documented in the sample label.

Sample Treatment

- Reasons for sample treatment:
- Concentration:
  - carried out when the concentration of the compound is too low to be detected by analysis method.
- Elimination of impurities:
  - added to the sample during the sampling procedure.
- Elimination of water:
  - indicate if the resulting data are referred to dry basis or wet basis.
- Homogenisation:
  - different results from sedimented and non-sedimented wastewater sample; composite samples should be well mixed.
- Dissolution:
  - improve performance of the analytical method.
- Elimination of interference:
  - compounds that increase or decrease the reading of the determinant of interest.

Sampling

- Different methods can give variable results of the sample. The analytical method to be used is depending on a number of factors, including:
  - suitability;
  - availability;
  - economy.
- National or international standards should be used.
- Laboratory carrying out the analysis could be accredited under appropriate standards, e.g. EN4500. [1]

Reporting

- From the large amount of data generated when a parameter is monitored, a summary of the results over a certain period of time is to be presented to the relevant authorities.
- Averages can either be peak of an hour values or averages of a calendar day, monthly or annual averages.

Basis on which data should be reported:

- Test environmental and technical performances of processes and (gas) cleaning techniques - hourly average, but when peak concentrations are very important, the average time has to be reduced; emissions expressed as mg/m^3;
- General compliance checking or the BAT-performance - use “emission relevant parameters” (ERP`s);
- Actual burden to the local environmental - emissions expressed kg/h;
- Emissions registration purpose-parameters expressed as tone/year;
- Comparing process performances-emissions as kg/tone of product.

Particle monitoring

Procedures for monitoring particulates are different from those of sampling other parameters, mainly because particulates are an inhomogeneous suspension in the gas stream.

A preliminary test should be done to check the suitability of the sampling plane.

Velocities and temperatures are measure in a number of points to test homogeneity.

The number of sampling points and the distribution of them is very important and it recommended that the number of points is not less than 4, with two perpendicular sampling lines.

The duration of the sampling depends on a number of factors, including the concentration of particles and the accuracy of the weighing.

To ensure representativeness of the sample, providing the wide range of particle size, it is necessary to sample is kinetically.

Equipment includes:

- sharp sampling nozzle;
- sampling flow rate measure;
- a particle separator (a cyclone, a filter or both).

Continuous gas monitoring classification:

Extractive systems - the gas is extract from the stack continuously along a sampling line, transported and conditioned before entering the analyser unit. The sampling point should be selected so that it is representative of the gas stream;

In-situ systems- The measuring cell is the duct itself; they are based on a beam of a certain wavelength that crosses the duct and it is attenuated proportionally to the concentration of the compound.

Aspects of a manual monitoring gas:

- Sampling time;
- Sampling time/contamination level;
- Flow rate control;
- Stability of the sample;
- Parameters to measures while sampling.

Devices of the equipment sampling:

- Flow measurement device to calculate exact the volume of the flow sample;
- Pump to extract the sample;
- Sample collector (absorption by solutions; adsorption on fine solids; cooling techniques; sample bags; personal sampler pumps). [3]

Waste water

Flow measurement is of great importance in order to calculate loads of pollutants to the receiving waters (error of <5% has been recommended; open and closed channels).

Aspects to taken into account:

- sampling method;
- nature of the sampler;
- conservation of the sample.

Sampling Method

Situations respecting industrial discharge:

- Effluent has a constant compositions over the day - a single sample can do;

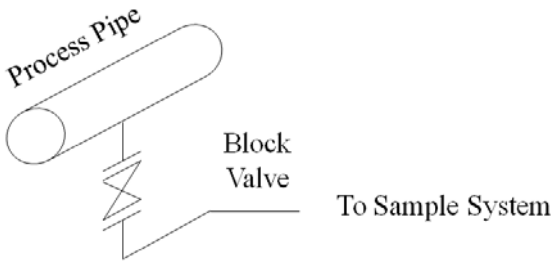

Figure 2. The sampling point in a pipe

- Composition Composition varies but the flowrate is constant - composite a sample by putting the same quantity every certain time, ex. every hour;
- Flowrate and composition varying - samples for the composite sample can be proportional to the flowrate;
- Parameters that change with time, for example the pH - measure periodically the value in the discharge. [2]

Nature of the Container

Types of suitable container materials for sampling purpose:

- Borosilicate glass;
- Plastic containers;
- Stainless Steel containers.

Conservation of the Sample

There are compounds that must be determined in-situ.

Others must be preserved until the moment of analysis by:

- low temperature;
- adding chemical reactants.

Sampling Point

Sewage samples can be taken from the source point before being mixed with other sewage and/or discharge into the river.

Sufficient space is in order to set up automatic sampling equipment.

Take samples on an outflow proportional or time proportional basis at the sewage treatment plant inlet and outlet. [2]

General considerations to account:

- Indicate for any sample aspect, color, odor, etc.;

- Take several samples, during the day, at night, different seasons, etc.;
- If a composite sample is taken, the sampling will be proportional to the flow rate;
- Carry out some in-situ determinations;
- Transport the samples cooled, so that temperature is kep low.

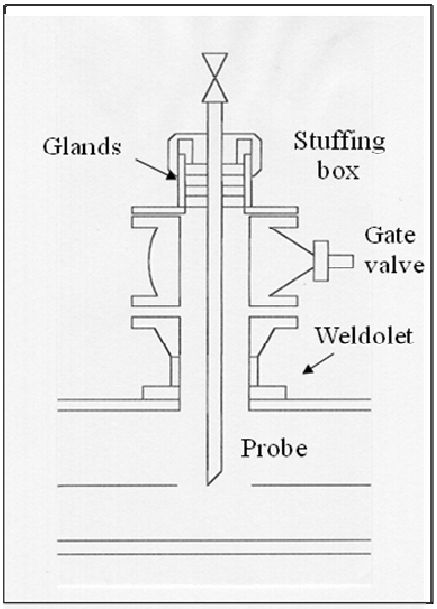

Figure 3. Probe for sampling in a pipe

Wastes

Sampling of Solid Material

Automatic samplers - movement of a collecting device, with a cutter, through a stream of material as it falls from a conveyor or a pipe;

Manual sampling: dry solid - made by coning and quartering.

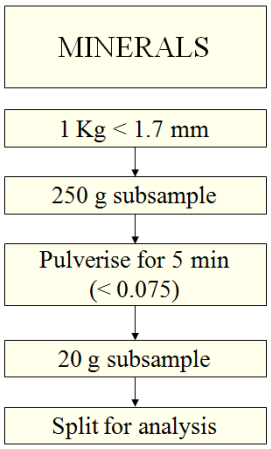

Figure 4. Sampling for chemical analysis of minerals

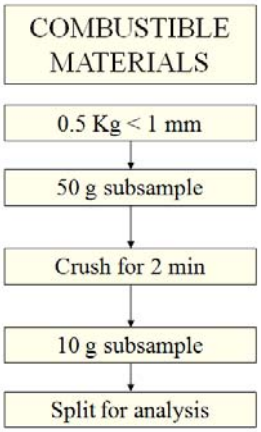

Figure 5. Sampling for chemical analysis of combustible minerals

Sampling of Wet (pulp) Material

Automatic samplers - a pneumatically operated piston is immersed directly into the pipeline preferably in vertical flow, with the piston in the "open" or "closed" position;

Manual sampling - material homogeneous in the storage vessel.

Level of Uniformity

For non-homogenous materials it is necessary to have several sampling points in order to obtain a representative sample.

The type of container, the amount of sample required and the number of subsamples needed, is depending on the size of the container (<200 litres or >200litres).

The type of analysis and the objectives of the monitoring also affect the sampling method for wastes.

3. ERRORS IN QUANTITATIVE ANALYSIS

Accuracy and precision

All measurements are accompanied by a certain amount of error and an estimate of its magnitude is necessary to validate results. The error cannot be eliminating completely, although its magnitude and nature can be characterized. It can also be reduce with improved techniques. In general, errors can be classified as random and systematic. If the same experiment is repeated several times, the individual measurements cluster around the mean value. The differences are due to unknown factors that are stochastic in nature and are termed random errors. They have a

Gaussian distribution and equal probability of being above or below the mean. On the other hand, systematic errors tend to bias the measurements in one direction. Systematic error is measured as the deviation from the true value.

Accuracy

Accuracy, the deviation from the true value, is a measure of systematic error. It is often estimated as the deviation of the mean from the true value:

$$\text{accuracy} = \frac{\text{mean} - \text{true value}}{\text{true value}} \quad (1)$$

The true value may not be known. For the purpose of comparison, measurement by an established method or by an accredited institution is accepted as the true value.

Precision

Precisions a measure of reproducibility and is affected by random error. Since all measurements contain random error, the result from a single measurement cannot be accepted as the true value. An estimate of this error is necessary to predict within what range the true value may lie and this is done by repeating a measurement several times [5]. Two important parameters, the average value and the variability of the measurement, are obtain from this process. The most widely used measure of average value is the arithmetic mean, $\bar{x}$:

$$\bar{x} = \frac{\sum x_i}{n} \quad (2)$$

where $\sum x_i$ is the sum of the replicate measurements and n is the total number of measurements. Since random errors are normally distributed, the common measure of variability (or precision) is the standard deviation, σ. This is calculated as

$$\sigma = \sqrt{\frac{\sum (x_i - \bar{x})^2}{n}} \quad (3)$$

When the data set is limited, the mean is often approximated as the true value, and the standard deviation may be underestimated. In that case, the unbiased estimate of σ, which is designated s, is computed as follows:

$$s = \sqrt{\frac{\sum (x_i - \bar{x})^2}{n-1}} \quad (4)$$

As the number of data points becomes larger, the value of s approaches that of σ. When n becomes as large as 20, the equation for σ may be used. Another term commonly used to measure variability is the coeffcient of variation (CV) or relative standard deviation (RSD), which may also be expressed as a percentage:

$$\text{RSD} = \frac{s}{\bar{x}} \quad \text{or} \quad \text{RSD} = \frac{s}{\bar{x}} \times 100 \quad (5)$$

Relative standard deviation is the parameter of choice for expressing precision in analytical sciences.

Precision is particularly important when sample preparation is involved.

The variability can also affect accuracy. It is well known that reproducibility of an analysis decreases disproportionately with decreasing concentration [6]. A typical relationship is shown in Figure 6, which shows that the uncertainty in trace analysis increases exponentially compared to the major and minor component analysis. Additional deviations to this curve are expected if sample preparation steps are added to the process. It may be prudent to assume that uncertainty from sample preparation would also increase with decrease in concentration. Generally speaking, analytical instruments have become quite sophisticated and provide high levels of accuracy and precision. On the other hand, sample preparation often remains a rigorous process that accounts for the majority of the variability.

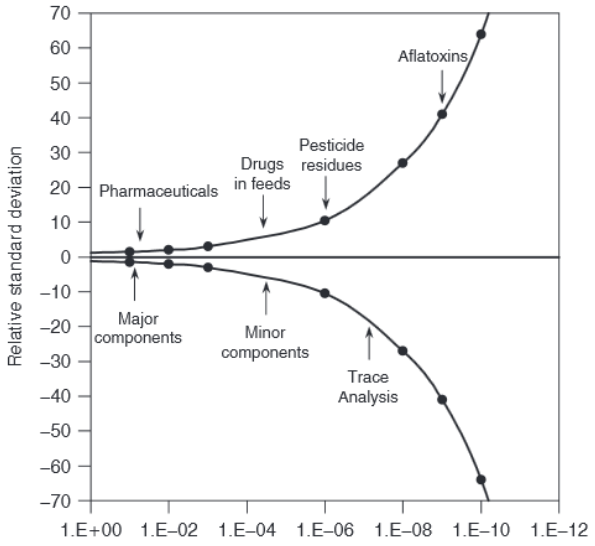

Figure 6. Reproducibility as a function of concentration during analytical measurements.

Going back to the example of the measurement of pesticides in fish, the final analysis may be carried out in a modern computer-controlled gas chromatograph/mass spectrograph (GC-MS).

The relative contribution of sample preparation depends on the steps in the measurement process. For instance, typically two-thirds of the time in an analytical chromatographic procedure is spent on sample preparation. An example of the determination of olanzapine in serum by high performance liquid chromatography/mass spectroscopy (HPLC-MS) illustrates this point [7]. Here, samples were mixed with an internal standard and cleaned up in a solid-phase extraction (SPE) cartridge. The quantization was done by a calibration curve. The recovery was 87G4% for three assays, where as repeatability of 10 replicate measurements was only 1 to 2%. A detailed error analysis [7] showed that 75% of the uncertainty came from the SPE step and the rest came from the analytical procedure. Of the latter, 24% was attributed to uncertainty in the calibration and the remaining 1% came from the variation in serum volume. It is also worth noting that improvement in the calibration procedure can be brought about by measures that are significantly simpler than those required for improving the SPE. The variability in SPE can come from the cartridge itself, the washing, the extraction, the drying or the red is solution steps. There are too many variables to control. Some useful approaches to reducing uncertainty during sample preparation are given below.

3. CONCLUSION

Environmental pollutions due to the anthropogenic pressure in the last century and mainly as result of obtaining the energy, from chemical industry, extractive metallurgy, transportation, burning or storing waste of any kind.

The monitoring system is based on the national monitoring subsystems, including elements of these subsystems.

Therefore, monitoring has become an information system with multiple special destinations, which is able measure the degree of impairment an thropogenic ambience, the future adverse effects.

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MONITORIZAREA MEDIULUI

Rezumat: Monitorizarea mediului reprezintă un ansamblu de acţiuni de supraveghere, prognoză, avertizare şi intervenţie care are în vedere evaluarea sistematică a dinamicii caracteristicilor calitative ale factorilor de mediu, în scopul cunoaşterii stării de calitate şi a semnificaţiei ecologice a acestora, evoluţiei şi implicaţiilor sociale ale schimbărilor produse, urmate de măsurile ce se impun. Monitorizarea implică ca posesorul permisului să facă măsuratori ale parametrilor şi condiţiilor de proces, verificarea datelor comunicate despre proces, nivelul indicatorilor de calitate a mediului şi raportarea rezultatelor la autoritatea de reglementare, în conformitate cu legile, reglementările sau permisele în vigoare.

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