Introduction

Odours perceived in the vicinity of an industrial plant, although generally considered as having no direct impact on the health of the neighbouring populations, have a detrimental effect on well being and, in turn, may indirectly lead to diseases... It is thus necessary to reduce as far as possible the odour levels in the environment. This is a difficult task that generally starts with source characterisation, which means:

– identifying the sources emitting odorous compounds;

– measuring the odour fluxes and ranking the sources according to this parameter in order to define treatment priorities;

– identifying the type of the odorous compounds to eliminate in order to select the best-suited odour abatement technology.

Answering these questions is not straightforward and requires the application of specific sampling and analytical methods for the identification of odorous compounds and quantification of the emissions.

Sources identification

There are several types of potential sources in an industrial plant:

– collected waste gases streams discharged through an elevated stack;

– point sources generating very intense odours in their immediate vicinity (vents, sumps, leak on a pipe...);

– large sizes equipments like decanters, basins... where specific emissions are rather low but which can be a significant source of nuisances due to the high exchange area with the atmosphere;

– episodic ancillary operations like cleaning, purging... or incidents of operations that may cause sudden and important odour emissions...

It is particularly important to stress that carefully examining the plant and its operating conditions is a prerequisite before starting any analysis campaign. In addition, our experience shows that funding a diagnosis on measurement carried out in the immediate vicinity of the equipments leads to an overestimation of the contribution of point sources and, on the contrary, to an underestimation of the surface sources. In that case, ancillary operations are also often ignored and stack emissions whose effect is perceived only at a certain distance of the plant are not taken into account.

Thus, in the first phase of the diagnosis, no source should be ignored or a priori considered as no significant. One must be as exhaustive as possible.

Flux determination

The impact of a plant on its surroundings can be evaluated only if the fluxes of odorous substances emitted by the various sources are known. That means that in addition to concentrations, odour laden airs flows must be measured in order to enable calculating the flux as the product of concentrations by the flow. This is quite easy when the odorous gases are collected and discharged through a stack. It is
much more difficult when the source is either a non-collected point source (vent, leak...) or a surface source (pond, settler...). In the latter case, measurement of concentrations in atmospheric air sample near the equipments can give only qualitative indications due to uncontrolled dilutions linked with local weather conditions. Another difficulty is connected with variations of odorous emissions. These variations are often very important although the process at the origin of the odorous emissions does not encompass such variability. As the perception of odours in the environment and the associated nuisance is more linked to variations than to a constant level, evaluating the variations at the source is very important. In addition, evaluating the variations and understanding their origin is generally the first step towards source reduction through modification of the process or of its management.

Fluxes measurement techniques applicable for different cases are briefly described below:

- Where the odours waste stream is collected, its flow can be measured in a duct or at the stack with classical methods like Pitot tube probing of a section, taking care that the measurement constraints are met (straight length, distance from upstream and downstream perturbations).

- When the source is located inside a building (for example a filter in a wastewater treatment plant...) and that there is no forced air extraction, the evaluation of the flow is quite difficult. The only technique available is gas tracing most commonly used gases for this purpose being sulfur hexafluoride and helium. Obtaining realistic results with this technique requires a careful examination of the process and of its immediate surroundings in order to optimise the implementation of the tracer gas generation system and of the sampling points. Specialists must take this up as well as in some cases, the application of 3D models for heat and mass flow simulation that may be useful to provide orientations for the design of a measurement campaign.

It must be stressed that the air flux from inside a building generally depends on weather conditions. This means that measurement must be carried out several times in order to cover a range of these weather conditions. That makes them very costly.

When the source is a surface artificially aerated from beneath, the specific airflow by unit of surface can be known with a fairly good precision. In this case, the flux measurement method consists in isolating a small area of the emitting surface with a chamber and measuring the concentration in the air flowing freely through the chamber. In that case, the specific flow at the surface is not modified by local wind conditions and can be considered equal to the aeration flow. Simply introducing a probe in the chamber performs sampling. Care must be taken that the sampling flow is much less than the airflow through the chamber. This method is applicable also to solid surfaces although more difficult due to the problem of sealing.

In case where the emitting surface is a calm, non-aerated surface (ponds, settlers, thickeners for example) the internal volume of the chamber is swept by a flow of pure air, in well-defined conditions. The sweeping flow is set at a value that provides for enough sampling capacity but does not influence the emission of odorous gases at the surface. The product of the concentrations in odorous substances by the sweeping airflow gives a picture of the specific flow of pollutants through a unit surface. It must be stressed that this technique does not allow the determination of the absolute pollutant flux since exchanges between the surface and the atmosphere largely depend on local wind speed and other weather related parameters. Nevertheless, provided that experimental conditions are kept identical, it is possible to compare fluxes emitted by different sources on the same site and to rank these sources accordingly.

**Analytical method**

It is rather trivial to say that the physicochemical analysis of an odorous gaseous stream is complex, in consideration of the hundreds of identifiable substances often present in those streams.

These substances are characterised by:

- a wide range of molecular weight, which may lead to problems of separation;
- a variety of different chemical functions, each one having a specific “odour quality”;
- a range of relative concentration, the most abundant substances being not in general the most important in term of odorous properties;
- a range of odour perception thresholds that may vary by several orders of magnitude.

This means that analytical methods applicable in this field must be very “powerful” and/or very specific.

Whatever the subsequent analytical method is, the first step is to take a gas sample. It is important to recall that the sampling time must be chosen in consideration of the variability of the emission, in order to be representative of different phases of the process.

The sample is then transferred to an analyser or to a capture device where the odorous substances are transferred to a solid or liquid phase where they keep stable.

Attention should be paid to the risk of “denaturation” of odour substances during gas sample transfer : some substances like H$_2$S are for example very reactive and can be lost through dissolution in the condenser....

That is why it is better to perform their capture and stabilisation or their analysis directly on site. If in certain circumstances it is absolutely necessary to take grab samples in a plastic bag care will be taken to avoid any
condensation on the walls of the bag and to carry out the analysis as soon as possible (less than 6 hours) after sampling. Even if these conditions are met, one must consider that the results are not quantitative (i.e. underestimated) for compounds like \( \text{H}_2\text{S} \).

The ideal situation is evidently to have available continuous specific analysis equipment on-site. This is possible only for reduced sulfur compounds, of particular importance in the field of odours in treatment stations and whose delayed analysis is complicated.

If a specific continuous analysis is impossible, the choice can be made between:

- a “global” sample with the most exhaustive possible laboratory analysis;
- a “specific” sample with subsequent analysis per “family” of pollutants [2].

In the case of odours arising from fermentation processes (agro-food industries, waste treatment stations, etc.) the second option has been preferred for a number of years. It furnishes essential information for guiding subsequent deodorising treatments and has the advantage of considerably overcoming the problem of compounds that complicate the “exhaustive” analysis and that are of little interest in terms of odours (divers hydrocarbons).

The combined use of exhaustive analysis methods often remains necessary, however, in order to detect the potential presence of other organic products that may be responsible for olfactory nuisances.

### Analyses per family

Malodorant pollutants possess particular chemical functions and in the case of odours arising from fermentation processes belong to the following four families:

- reduced sulfur compounds;
- ammonia and amines;
- aldehydes and ketones;
- organic acids.

In every case, the low molecular weight compounds within each family are analysed, since they are the most abundant, while verifying that sensitivity is of the same order as the odour perception thresholds.

### Reduced sulfur compounds

The products are analysed with a semi-continuous instrument, since there exist no chemical trapping and delayed analysis methods that enable the different compounds to be distinguished with the same sensitivity [3,4].

We use a TRACOR sequential automatic analyser operating by gas chromatographic separation followed by flame photometry detection. The instrument can be transported on-site and enables semi-continuous rapid analyses of the \( \text{H}_2\text{S}, \ \text{CH}_3\text{SH}, \ \text{C}_2\text{H}_5\text{SH}, \ \text{CS}_2, \ \text{dimethyl sulfide} \) concentrations to be carried out.

### Ammonia and amines

Bubbling through acid solution traps these compounds. Analysis of the solutions is carried out in the laboratory by gas chromatography coupled to an Nitrogen-Phosphorus detector (NPD), after introduction and neutralisation of the solution into the column, for aliphatic and aromatic amines [5], and by ion exchange chromatography with conductimetry detection for ammonia.

### Aldehydes and ketones

Aldehydes and ketones are trapped by bubbling in a solution of 2,4-dinitrophenylhydrazine (DNPH) in acid medium, or are adsorbed on an adsorbent coated with DNPH and phosphoric acid [6]. Analysis of their appropriate hydrazones is conducted in the laboratory using liquid chromatography and UV detection [7].

### Organic acids

Organic acids in polluted air are determined by trapping the compounds in a basic solution, followed by laboratory analysis by gas chromatography coupled with a flame ionisation detector (FID).

### Other compounds

In some circumstances, it may be useful to look for other odorous compounds like, for example, alcohols and nitriles in the foods industry, solvents in the printing or painting industry... These compounds are collected by sampling on solid sorbents like silica gel or polymers. They are desorbed with an organic solvent in the laboratory and analysed by gas chromatography coupled with a flame ionisation detector (FID).

**“Exhaustive” analysis**

This relatively old concept of taking a “global” sample of organic compounds and conducting a subsequent analysis with very powerful equipment (chromatography/mass spectrometry coupling) has been extensively studied.

The current trend is to conduct a trapping-concentration of pollutants contained in one to 10 liters of air in a small cartridge containing a chromatographic support (Tenax, Porapak, etc.). The totality of the pollutants trapped is subsequently desorbed thermally (and totally) very rapidly (flash desorption) onto a chromatographic column and is analysed by gas chromatography [8].

### Additional analyses

Usual practice is to measure the total content of gaseous organic products (total hydrocarbons or THC) in the air examined, using a flame ionisation analyser (french standard [9] or european standard [10]). This analysis furnishes a pollution index that is not directly interesting in terms of
odours, but it does enable sampling methodology to be controlled and variations in overall emissions in time or in space to be rapidly detected.

Examples of applications

The characterisation method described above has been successfully applied to different type of sources. The application to waste water treatment plants, where a large variety of sources including point, area and stack sources are encountered, has been described previously [11,12]. The application for stack gases characterisation has been developed in parallel and some examples are given hereafter.

Sludge drying and burning

Analyses described hereafter have been carried out to address a problem of complaints of populations living near a sludge drying and burning plant.

The continuous record, by an automatic analyser operating by gas chromatography coupled to a flame photometry detector clearly demonstrates that puffs of \( \text{H}_2\text{S} \) that may lead to odorous episodes in the vicinity of the plant, frequently occur. The anticorrelation between \( \text{H}_2\text{S} \) and \( \text{SO}_2 \) concentrations shows that bad combustion conditions are at the origin of the \( \text{H}_2\text{S} \) puffs. A careful inspection of the plant confirmed this interpretation and demonstrated that the oven feeding system was not functioning properly and delivered from time to time big aggregates of sludge which did not burn completely and generated \( \text{H}_2\text{S} \) emissions. Modifications of the feeding system made it possible to considerably reduce odour emission at a very low cost while improving equipment’s lifetime.

Composting unit

The aim of the study was to establish an inventory of the fluxes of malodorous compounds emitted by a domestic refuse composting plant. The principal conclusions of the diagnostic are presented below in a graphic form providing informations on:

– the hierarchic order of emission sources in such a plant;
– the physicochemical identification of the major compounds;
– the performances of the biofiltration deodorizing equipment.

Sugar extraction plant

Sugar extraction from sugar beets produces large amounts of wastewaters, which have a high odour emission potential. The objectives of the investigations carried out in a typical plant was to assess the relative contributions of two categories of wastewaters (“defoliage water”, used to wash the sugar beet during the defoliation process and “transport water”) in order to define a strategy of flux management and treatment for odour reduction. In addition to the odorous compounds that are systematically looked for (reduced sulfur compounds, organic acids, basic nitrogen compounds, aldehydes and ketones) two specific families of substances have been quantified: alcohols and nitriles.

The results are shown on figure 3. They confirm that the “defoliage water” is much more loaded than transport water.
which means that it is worth managing and treating the corresponding fluxes separately. Once the concentrations of the different odorous substances have been weighted by their odour perception threshold, the major contribution is attributable to the reduced sulfur compounds. However, the emissions of a large number of other highly odorous compounds like organic acids must be taken into account in the design of an odour abatement strategy.

**Assessment of odour abatement efficiency of neutralizers**

The methodology of physicochemical characterisation of odours has been applied to assess the odour abatement efficiency of “neutralizers”. Those are commercial products that are put into contact with odorous gas flows, either in a scrubber or pulverized into a duct or a stack. The claimed
The effect is not a masking one but a chemical one: the products are supposed to react with the odorous compounds and to neutralize the chemical function responsible for odour. To assess the efficiency of such a process, it is necessary to carry out simultaneously olfactometric [13,14] and physico-chemical characterisations.

Trials have been performed in three industrial plants:

**Site 1:** waste gases of a sludge-drying unit in a glucose production plant from cornstarch.

**Site 2:** onions drying waste gases.

**Site 3:** air extracted from a composting building.

As these products are always diluted in water before they are put into contact with the air flow and in order to make sure that the measured efficiency is really attributable to the product (and not to the dissolution of the odorous compounds in water) three successive trials have been performed on each site:

- no product or water addition (raw effluent);
- contact with water only;
- contact with water + product in normal use conditions recommended by the supplier.

As far as sampling is concerned, the possible presence of water droplets may cause problems for odour determination as well as for chemical analysis due to uncontrolled dissolution of odorous compounds in water. To avoid this situation, and when necessary, a diluting device using dry air has been operated for sampling.

**Site 1**

The analytical results are presented in figure 4.

The olfactometric results are given on the following table.

<table>
<thead>
<tr>
<th>Dilution to threshold factor</th>
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</thead>
<tbody>
<tr>
<td>Raw effluent</td>
<td>$5.26 \times 10^5$</td>
</tr>
<tr>
<td>Effluent + water pulverization</td>
<td>$5.89 \times 10^5$</td>
</tr>
<tr>
<td>Effluent + water pulverisation + product</td>
<td>$3.18 \times 10^5$</td>
</tr>
</tbody>
</table>

The analytical results show that the odorous compound concentrations are very high. Taking into account the fact that the trials have been conducted successively and owing to the variability of the concentrations during the course of a day, one cannot claim that the addition of the “neutralizing” agent has any effect compared to water only, except maybe as regards organic acids. Olfactometric levels that are not very different confirm this result.

**Site 2**

Industrial onions dehydration plants produce large amounts of odorous, water saturated waste gases. Extraction ports are distributed along the drying oven and connected to a number of stacks (17 for the 40 m long oven studied). The...
neutralization device has been installed for test on one of the stacks. The product has been injected in the waste gas flow in form of micronized droplets with a trifluid system/steam/air/product.

Three configurations have been tested:

- raw effluent;
- raw effluent + steam/air;
- raw effluent + steam/air/product.

The analytical results are presented on figure 5 (reduced sulfur compounds) and figure 6 (acids + VOC).

Olfactometric results are presented in the following table:
As far as the interpretation of the results is concerned, it is important to mention that concentration featured on figure 5 and 6 are averages over the measurement period while olfactometric results correspond to grab samples. When the emissions present large instantaneous variations as it is the case in this plant, comparison of different situations over time maybe difficult. That is why an increase in dilution to threshold factor in the water only situation may seem inconsistent with the large decrease in average concentrations of organic sulfur compounds as compared to the raw effluent situation.

Taking into account these considerations, the obvious conclusion is that the product has almost no measurable effect neither on odour level, nor on chemical composition of the effluent.

**Site 3**

The unit produces compost by accelerated fermentation of a mixture of industrial wastewater treatment sludges and barks. Air is extracted above the heaps and discharged through a stack. For the purpose of the test a part has been diverted and scrubbed with water containing the product in a device installed by the product supplier.

The analytical results are presented in figure 7.

The olfactometric results are given in the following table.

**Table II. Assessment of odour abatement efficiency of neutralizers in an onions deshydratation plant – Olfactometric results.**

<table>
<thead>
<tr>
<th>Dilution to threshold factor</th>
<th>Raw effluent</th>
<th>9 370</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw effluent + steam/air</td>
<td>13 490</td>
<td></td>
</tr>
<tr>
<td>Raw effluent + steam/air/product</td>
<td>7 140</td>
<td></td>
</tr>
</tbody>
</table>

In this case as in the previous ones, it is clearly demonstrated that the treatment by the “neutralizing” product is almost completely inefficient.

Although the results of this limited set of experiments should not be generalized, they are consistent enough to support the recommendation of carefully testing a product before deciding to use it as regards its effectiveness in chemical abatement as well in odour level reduction.

**Conclusion**

The main sources of odour on an industrial site are often determined empirically, based on the analysis of air sampled...
over the plants and on the intensity of odours perceived in their immediate vicinity.

This procedure is highly subjective, accords a disproportionate importance to intense but sporadic sources, and underestimates the effect of large-surface, diffuse sources.

It is thus absolutely necessary to use a more rigorous procedure and to correctly determine the fluxes of odorous products emitted by each plant category in order to define their relative contribution to nuisance in the vicinity.

These diagnosis can be established with air sampling procedures that are specific to surface sources, combined with very sensitive physicochemical analysis methods, as they have been discussed here:

– determination of the foul smelling compounds;
– identification and quantification of the different emission sources;
– functional optimisation of certain installations in terms of environmental emissions;
– orientation of a strategy of future treatment of malodorous effluents.

The physico-chemical characterisation methodology has been successfully applied in various types of industries and processes and proved very relevant in providing objective data on chemical substances involved and corresponding concentrations, upon which we can rely to design cost-effective abatement strategies.

References
The compositional analysis of heavy oil products has become a key step in various developments. However, the characterization of such species still remains a time-consuming work despite all the efforts already made in this field. The complexity of these oil matrices tends to increase with their boiling point. A large variety of compounds is present in terms of structures and number of molecules (Strausz and Lown, 2003). Numerous studies carried out on heavy products analyses were pri