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PTR-MS monitoring of odour emissions from composting plants

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Abstract

We studied the possibility of monitoring with proton transfer reaction-mass spectrometry (PTR-MS) odours emitted in various situations related to composting plants of municipal solid waste (MSW), i.e., waste storage, waste management, and biofilters. Comparison of PTR-MS volatile profiles of the gaseous mixtures entering and exiting a biofilter suggests the possibility of fast and reliable monitoring biofilter efficiency. Moreover, we investigated the relationships between the olfactometric assessment of odour concentration and PTR-MS spectral line intensity finding a positive correlation between the former and several masses and their overall intensity. The application of multivariate calibration methods allows to determine odour concentrations based only on PTR-MS instrumental data. The possibility of avoiding the use of time consuming and expensive olfactometric methods and applications in monitoring waste treatments plants and, in particular, of biofilters is suggested.

Keywords: Proton transfer reaction-mass spectrometry; Olfactometry; Multivariate calibration; Compost; Biofilter

1. Introduction

Many activities related to industry and agriculture are characterised by the emission of a large quantity of volatile compounds that can produce significant concentrations also at a far distance from their origin. The control of gaseous emissions is undoubtedly one of the most difficult problems in the composting practice [1]. Determination of gaseous emissions is important due to two different aspects, (i) a toxicological, often related to few specific and known substances that must be constantly controlled and maintained below fixed limits and (ii) an environmental, related to the perception of odour in the neighbourhood of the source. While the first issue has, obviously, always been taken into serious account and the toxicological properties of these substances carefully have been investigated and regulated by corresponding laws (e.g., threshold limit values or permissible exposure limits), the second one still presents several open questions. This is because our nose is often very sensitive even to low concentrations and because the physiological odour perception is a complex process that produces a response that is a non linear, partly subjective, and mostly an unknown function of the concentration of compounds reaching our nose [2]. In general the odour related issues arise already before the toxicological ones, because the odour recognition concentration is usually much lower than the threshold limit values (e.g., for acetaldehyde the first is 549 $\mu g/m^3$ and the second 180 000 $\mu g/m^3$). There are studies indicating possible effects of odour on public welfare and law-makers must take into account the compliance of people living close to potential source of odour [3]. Up to now olfactometry seemed to be

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the most direct and reliable tool to assess the real impact on people of single compounds or complex mixtures and has been more and more recognised as the reference method in many countries with specific normative indications, e.g., VDI norms in Germany, AFNOR in France, ASTM in the USA [4].

Its main advantage, the direct measure of the human response to olfactory stimuli, is also a severe drawback for olfactometry: it uses the human noses. The analyst must find, select and train people. The 'instrument' is thus expensive, not always available, its use is time-consuming and not possible if the presence of toxic compounds is suspected. Moreover, it is not suitable for on-site measurements or continuous monitoring and the expected error in a single run determination can be, in our experience, quite high. If and how a panel of few people can be representative of the total population is also questionable. Despite these shortcomings, odour panel techniques are a valuable, perhaps necessary, tool for the very difficult task of quantifying environmental odour concentrations [5].

Among the alternative methods, gas-chromatographic measurements of gas mixtures are also in general not rapid and simple enough [6] and the cheaper electronic noses don't yet seem sensitive and accurate enough [7]. Applications to odour control show, in general, poor correlation with olfactometry results thus indicating a lack of sensitivity for many important compounds and apparently good models are probably overfitted and do not show validating data [8].

Many classes of compounds are potentially relevant in the composting process because they are present both in the initial waste and as intermediate and final products of biochemical metabolic pathways. For instance fatty acids often hydrolysed to their short chain forms (acetic, propionic and butyric acids), in general readily degradable, amines and ammonia produced in anaerobic decomposition of proteins and aminoacids, aromatic compounds present in many wood species and formed by lignin breakdown (wood decomposition) and hydrogen sulphide which is a very strong source of odour and is, in general, formed in anoxic condition. Organic sulphides (mercaptanes) formed both in anaerobic and aerobic conditions but in presence of oxygen oxidised to dimethyl sulphide and dimetyl disulphide, and terpenes mostly induced in composting plants by the presence of wood and plants [9,6]. Many other compounds can, however, be present and also contribute to the odour of composting plants and their possible presence and relative significance must be considered.

Biofiltration exploits microbial metabolic reactions to treat contaminated air. The contaminants are absorbed from a gas to an aqueous phase where microbial attack occurs. Through oxidizing and occasionally reducing reactions, the contaminants are converted into carbon dioxide, water vapour, and organic biomass. Many variations of this technique have been proposed and widely used particularly in the USA and Europe, in particular in the Netherlands and Germany [10].

In a previous study we compared proton transfer reaction-mass spectrometry (PTR-MS) analysis with sensory characterisation of food: we noticed that product separation through multivariate analysis of PTR-MS spectral fingerprinting is comparable to the separation obtained by descriptive [11] or discriminative [12] sensory analysis. More recently, we proposed the possibility of calibrating instrumental data with sensory data to estimate sensory attributes (odour and aroma) only by PTR-MS data [13]. Based on this success, we applied here for the first time PTR-MS as an alternative method to olfactometric measurements of samples collected during the different stages or phases of the composting plants.

2. Materials and methods

2.1. Samples

Samples have been collected in Nalophan NA© bags from three different composting plants in northern Italy with the aim of covering as many different situations as possible: biofilter inlet and outlet, treated and untreated, fresh and old waste heaps, etc. For punctual sources (e.g., ducts) gaseous samples have been directly inflated in the bags. For distributed sources (e.g., surface of biofilters) suitable sampling was performed via static methods following CEN directives [14]. Table 1 gives a detailed description of the samples.

Samples have been collected on different days, preserved at room temperature and protected from light exposure. Samples referring to the comparison of the biofilter inlet and outlet in Castiglione delle Stiviere (Italy) were taken on the same day. Measurements, both olfactometric and by PTR-MS, were performed within 24 h from sampling.

2.2. Olfactometric measurements

Measurements were carried out with a 4-booth olfactometer (TO7 model, ECOMA GmbH, Germany) where dilution steps, data collection and estimates of odour units are computer controlled. A sequence of air samples of decreasing dilution (increasing intensity), randomly mixed with blank samples (clean air), are sent to the four panel members. The sequence stops when all panel members correctly recognise two successive dilution steps. By the definition for the odour unit (OU) it follows that the sample concentration (OU/m^3) is the number of dilutions necessary to let 50% of the panel correctly recognise the stimulus [14].

Results in OU/m^3 are in Table 1. Typical errors for olfactometric determination can be, in our experience, quite high and the possibility of errors up to 50% or more must be taken into account. Literature data available, even if somehow unclear or not easily comparable, are showing similar results [4,6,15].

Table 1
Samples description

Sample	Plant location	Description	Odour concentration (OU/m^3)
N1	Naturno (Bolzano, Italy)	Just prepared windrow: 40% of organic fraction of MSW and 60% of dead branches	24000
N2	Naturno (Bolzano, Italy)	Windrow (oxidising, covered by gore-tex, 20 days old): over the cover	750
N3	Naturno (Bolzano, Italy)	Windrow (oxidising, 20 days old): after cover removing	3400
N4	Naturno (Bolzano, Italy)	Maturing windrow (55 days)	1300
N5	Naturno (Bolzano, Italy)	Mature compost windrow (before sieving, more than 90 days old)	1300
N6	Naturno (Bolzano, Italy)	Starting compost pile: 100% organic fraction of MSW	5700
I1	Ischia Podetti (Trento, Italy)	Composting plant: air from the biofilter[a]	840
I2	Ischia Podetti (Trento, Italy)	Composting plant: air from the biofilter[a]	2700
I3	Ischia Podetti (Trento, Italy)	Composting plant: air from the biofilter[a]	2100
I4	Ischia Podetti (Trento, Italy)	Composting plant: air from the biofilter[a]	4200
I5	Ischia Podetti (Trento, Italy)	Composting plant: air from the biofilter[a]	1900
I6	Ischia Podetti (Trento, Italy)	Composting plant: air from the biofilter[a]	780
I7	Ischia Podetti (Trento, Italy)	Old MSW deposit: biogas biofilter	290
I8	Ischia Podetti (Trento, Italy)	Old MSW deposit: old pile	940
I9	Ischia Podetti (Trento, Italy)	Old MSW deposit: old pile	890
I10	Ischia Podetti (Trento, Italy)	Old MSW deposit: old pile	6700
I11	Ischia Podetti (Trento, Italy)	Old MSW deposit: percolate tank	140
I12	Ischia Podetti (Trento, Italy)	Old MSW deposit: percolate tank	140
I13	Ischia Podetti (Trento, Italy)	Old MSW deposit: old pile	170
I14	Ischia Podetti (Trento, Italy)	Old MSW deposit: old pile	57
I15	Ischia Podetti (Trento, Italy)	Old MSW deposit: heap of waste and earth	13000
I16	Ischia Podetti (Trento, Italy)	Old MSW deposit: air from the biogas biofilter	>256000[c]
I17	Ischia Podetti (Trento, Italy)	Old MSW deposit: old pile	67
C1	Castiglione delle Stiviere (Mantova, Italy)	Composting plant: air exiting the biofilter[b]	–
C2	Castiglione delle Stiviere (Mantova, Italy)	Composting plant: air exiting the biofilter[b]	–
C3	Castiglione delle Stiviere (Mantova, Italy)	Composting plant: air exiting the biofilter[b]	–
C4	Castiglione delle Stiviere (Mantova, Italy)	Composting plant: air exiting the biofilter[b]	–
C5	Castiglione delle Stiviere (Mantova, Italy)	Composting plant: air entering the biofilter[b]	–
C6	Castiglione delle Stiviere (Mantova, Italy)	Composting plant: air entering the biofilter[b]	–

[a] Samples collected at different points and times over the same biofilter (TN).
[b] Samples collected at 12 different sites on the same biofilter (MN) on the same day. Every bag contains the volatile mixtures of three different sites.
[c] The odour concentration of this sample is above the dilution possibility of the used olfactometer.

2.3. PTR-MS analysis

For a description of the PTR-MS technique we refer to [16]. The instrument used for this study is a standard commercial PTR-MS (Ionicon Analytik GmbH, Innsbruck).

Less than 4 h after the olfactometric measurements, 10 sccm of the gas mixture remaining in the Nalophan© bags were directly extracted with a stainless steel needle connected to the PTR-MS drift tube by a Teflon tube heated to 65 °C. Spectra have been collected from m/z = 20 to m/z = 240 and the average of five spectra were used to characterise the samples. For samples C1–C6 we have six repetitions. Approximate concentrations in ppb were obtained using the relation reported in [16] assuming for convenience a constant reaction rate of 2×10^{-9} cm^3/s for all masses. The systematic errors induced by different reaction rate constants (typically below 20% but possibly higher) must be taken into account when comparing our data with other publications but these rather large error bars are not relevant for the following analysis.

2.4. Data analysis

Besides basic data analysis and visualisation by standard software, the preliminary statistical analysis on the data matrix obtained (computation of statistical moments and correlation matrices) and ordinary least square linear regressions were carried out using the Statistica 6.0 package (StatSoft, Inc., San Diego, CA, USA). PLS Toolbox 3.0 for Matlab (Eigenvectors, Inc., Seattle, WA, USA) was used in the multivariate calibration step involving the building of a partial least squares (PLS [17]) model to correlate the PTR-MS intensities to the olfactometric results. PLS is the most commonly used chemometric method to build a linear multivariate model, as it can deal with a large number of highly co-linear and noisy variables. Moreover, this technique can also be used when there are more variables than samples, as often happens in the case of spectroscopic or spectrometric data.

A partial leave-one-out cross-validation [18] procedure was used to assess the predictive ability of the calibrated model. It consists of using in turn all the samples but one to build the calibration model and to compute the error score

using the remaining sample. So every sample is used once as an 'unknown' to validate the model. An example of multivariate analysis on PTR-MS spectra for discrimination purposes can be found in [19]. Here we concentrate on the calibration problem.

3. Results and discussion

A preliminary indication of the usefulness of PTR-MS analysis can be obtained by the comparison of spectral intensities of samples collected upstream and downstream a biofilter used to reduce the concentration of volatile compounds responsible for odour in the air exiting a composting plant. As an example the average signals and the maximal errors of the low mass section of PTR-MS spectra of the samples collected before the biofilter (samples C5 and C6) and after it (samples C1–C4) are shown in Fig. 1. A reduction in the signal intensity for many masses is evident and only a few masses have significantly higher intensities downstream the biofilter. Among these, e.g., mass 61 and 43, are due to acetic acid and to common fragments of many compounds, mostly alcohols and esters [20], present also in wood chips or bark, usually found in biofilters. Though we do not have enough information for a complete interpretation (identification) of the mass spectra, it is worth noticing that many masses which are reduced can be tentatively related to compounds that have been reported as important in composting plants and that have rather low odour threshold, e.g., mass 45 for acetaldehyde, mass 49 for methylmercaptane, mass 63 for dimethylsulphide and few other organic sulphur compounds, etc. It is reasonable to expect that the more the biofilter loses its efficiency the more the spectra measured at the inlet and at the outlet should be similar in intensity; real-time monitoring by PTR-MS provides a tool to control thus on-line the biofilter efficiency.

In general PTR-MS results can be used as a reliable estimate of the maximum possible concentration of a compound and this is important for industrial plant control or to complement the studies that try to follow the process of compost maturation. A detailed comparison of PTR-MS and GC measurements for quantification of these effects will be published, for different samples, elsewhere.

Let us now consider the subset of samples in Table 1 for which odour concentration measurements are available and consider the relation between olfactometric measurements and PTR-MS spectral intensities. In a first attempt we have plotted (see Fig. 2) the total concentration (adding up all ions from m/z = 33 to m/z = 200, excluding m/z = 37 and m/z = 38 that should be related only to humidity) against the olfactometric unit for all samples given in Table 1. The use of logarithmic scale seems convenient not only because of the spread of the data over several orders of magnitude but also because physiological mechanisms are non-linear and usually described by power laws [21]. Even if the simple second order polynomial fit (line in Fig. 2) cannot describe accurately all points (some of them are quite distant from the fit) the presence of a correlation is evident. Much better correlation can be found if we consider samples collected in the same location and of similar type or coming from the same plant: this is reasonable but less interesting if we intend to develop a model suitable to predict unknown samples. Even if a simple linear model (on a log–log graph) is not likely to be good for such a complex problem, overall correlation between the logarithm of PTR-MS total intensity and that of olfactometric intensity is quite good (R^2 = 0.8 for an apparent linear fit) and the logarithms of many masses are positively correlated with log (OU/m^3). We notice that correlation is not simply a matter of intensity because, e.g., mass 137 and mass 81 (typically terpenes) are the most intense ones and they are always present (in ppm range) but they show poor correlation with the olfactometric intensity. The reason for this being that samples of different origin have also different composi-

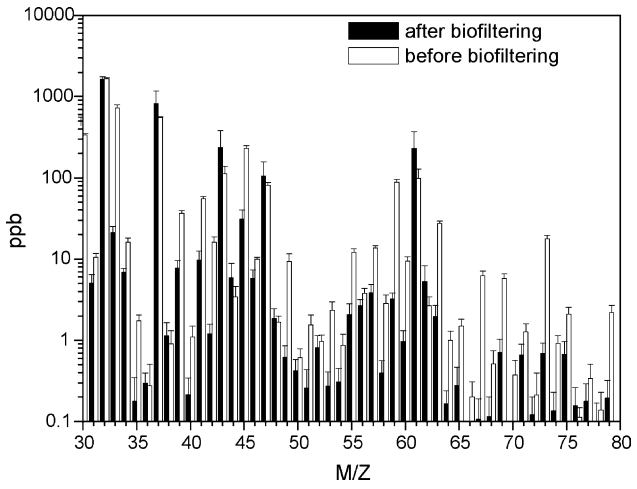

Fig. 1. Comparison of PTR-MS spectra measured before (white) and after a biofilter (black).

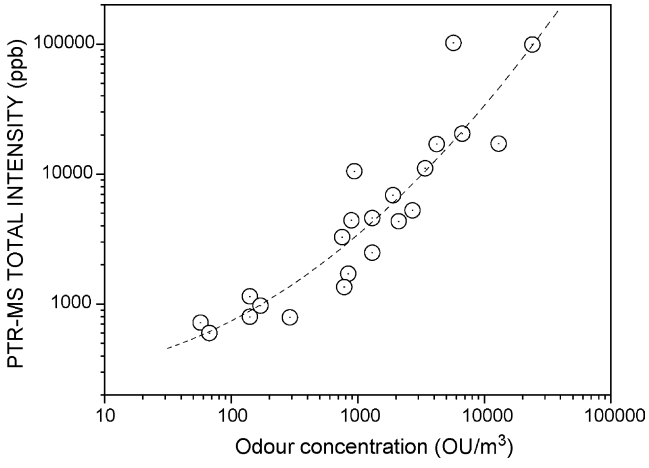

Fig. 2. Plot of the total VOCs concentration for $m/z\in$ (33; 200) as measured by PTR-MS vs. the odour concentration evaluated by olfactometry. The line indicates an apparent fit with a second order polynomial.

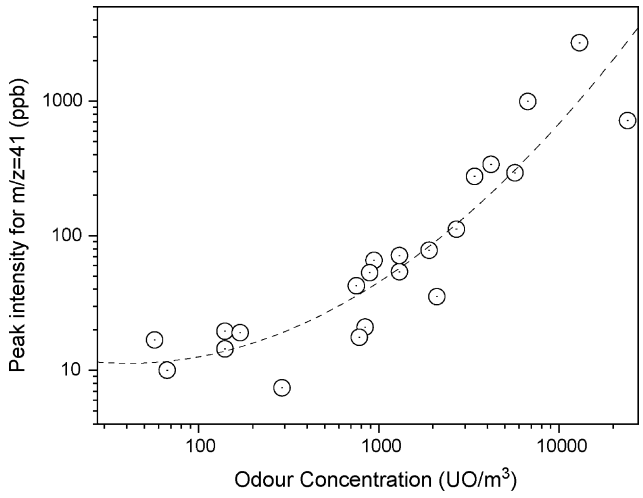

Fig. 3. Intensity of the PTR-MS signal at $m/z = 41$ vs. the odour concentration evaluated by olfactometry. The line indicates an apparent fit with a second order polynomial.

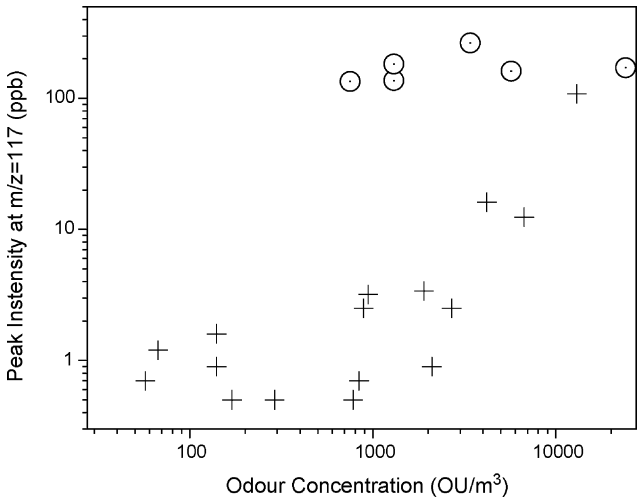

Fig. 5. Intensity of the PTR-MS signal at $m/z = 117$ vs. the odour concentration evaluated by olfactometry. Sample N1–N6 are indicated by circles.

tion and a simple monovariate linear regression is not able to appropriately consider the interaction of all signals. As an example let us consider a few representative cases. Mass 41 is related to the fragmentation of many classes of compounds and is not selective but most likely an indication of the global intensity, in fact its behaviour (Fig. 3) resembles that of the total intensity in Fig. 2. Mass 49 (very likely related to methylmercaptane, Fig. 4) shows a quite different behaviour for samples N1–N6 and I1–I6 (in both cases though an almost linear relation to odour units is evident), whereas for the other samples mass 49 does not show any correlation. Furthermore mass 63 connected to other sulphur compounds (dimethylsulfide, ethylmercaptane) shows similar trends. Finally mass 117 (molecular peak or fragment of several esters, Fig. 5) is an example of a mass that is characteristic of the samples collected in one location (circles in Fig. 5) and is not, for these samples, clearly related to odour concentration. In general, however, odour concentration appears to correlate with overall spectral intensity and with several specific masses. It is thus worth trying to perform a more accurate and powerful statistical analysis to understand if we can reliably predict from PTR-MS analysis the intensity of odour as perceived by humans and measured by olfactometry.

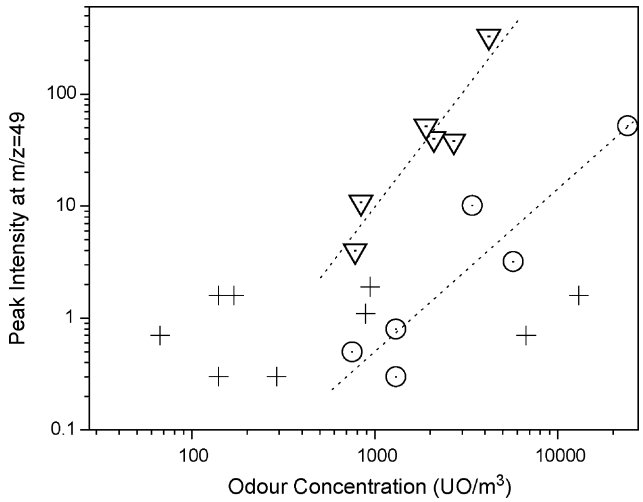

Fig. 4. Intensity of the PTR-MS signal at $m/z = 49$ vs. the odour concentration evaluated by olfactometry. Sample I1–I6 are indicated by triangles and N1–N6 by circles. Dotted lined indicates apparent linear fits on these subset of samples.

As described above, PLS regression was used to build a calibration model able to relate the analytical results from PTR-MS spectrometry to the olfactometric scores measured for the samples. Both the predictor data matrix (containing PTR-MS intensities) and the dependent variable (olfactometric scores) have been autoscaled, before PLS. In a first attempt we carried out a PLS1 analysis to relate the olfactometric data (dependent variable) to the PTR-MS spectral intensities (independent data). The best model (chosen as a compromise between the number of latent variables to be included and its RMS error of regression) is obtained with four PLS latent variables and accounts for 48% of the variance in the X space and 97.70% in the Y space. A comparison between the predicted and the measured odour concentration is shown in Fig. 6. The main problem is that the data points are not distributed regularly and this can seriously affect the analysis. As mentioned above a more reliable and realistic training/trial data-set is obtained using the logarithms of the odour intensities. This should provide a better data distribution and a more realistic imitation of physiological processes. In this case the optimal model, which is obtained including two latent variables only, accounted for 66% of X and 93% of the Y variance, respectively. A summary is presented in Fig. 7: data are always predicted with an accuracy of over 50%, with only the two points with a measured intensity of 57 and 67 OU/m^3 having an error of about 100%. Because of the intrinsic uncertainty of olfactometric methods we should not expect a better agreement (a better agreement would be suspicious and

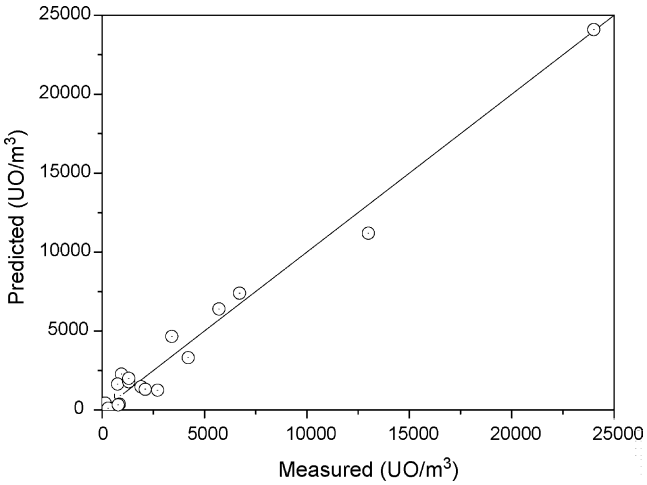

Fig. 6. Odour concentration predicted by PTR-MS data vs. the measured olfactometric intensity. The PLS prediction is based on four latent variables has been developed on the row data.

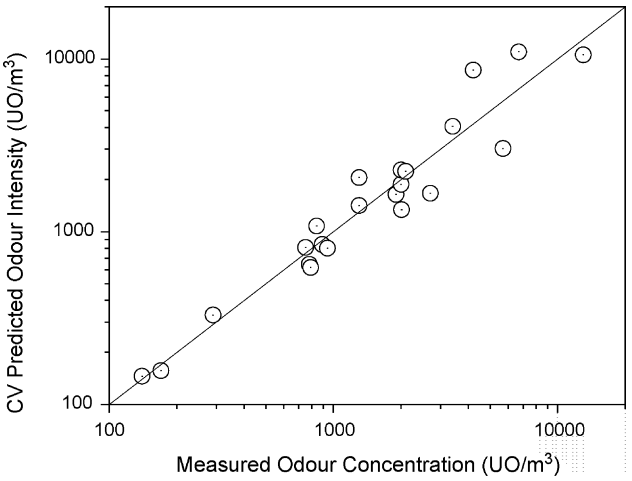

Fig. 8. Cross validation of the PLS model developed with the logarithms of the data using three latent variables (see text).

indicate the presence of overfitting). The presence of higher errors (see Fig. 7) in the case of low intensity samples does not seem critical because they are very close to the typical background level (20–30 OU/m^3) and thus close to the lowest detection limit of olfactometry. We notice that the current trend is to request a value of 300 OU/m^3 at the outlet of a biofilter [22].

As a final proof of the usefulness of the proposed method for odour control by PTR-MS, we present the result of a modified cross-validation approach to evaluate if the model constructed is able to predict the odour concentration of an unknown sample based on the PTR-MS measurement. As reported above, the samples corresponding to the lower odour intensities are not described accurately while the sample with the highest olfactometric score is not reliable (just an overrange indication by olfactometric measurements). Moreover, the literature on the use of cross-validation methods for calibration shows that the leave-one-out procedure is particularly sensitive to the extreme values and outliers [23,18]. These considerations, together with the small number of samples, which could not allow the use a training/test splitting, led us to validate the predictive model by applying a 'reduced' leave-one-out cross-validation, where the samples corresponding to the extreme values of the olfactometric intensities have not been considered for testing.

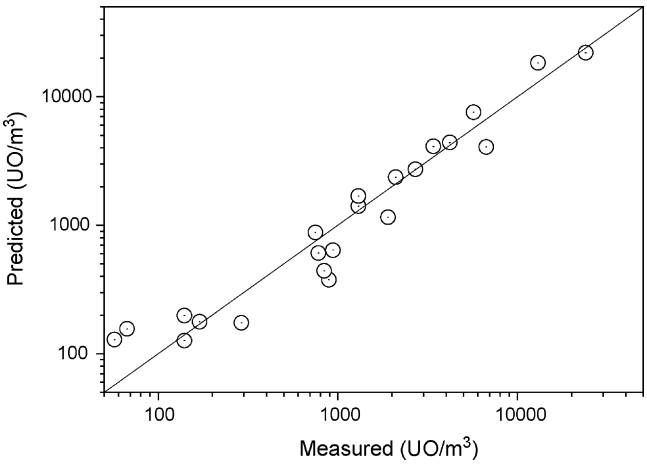

Fig. 7. Odour concentration predicted by PTR-MS data vs. the measured olfactometric intensity. The PLS prediction is based on two latent variables and has been developed on the logarithms of the data.

We thus report in Fig. 8 cross-validated data (that is the value that the model proposes without knowing the real odour concentration as measured by olfactometry) on the sample remaining after elimination of extreme samples. Fig. 8 clearly shows that predictions of the odour concentration estimation by PTR-MS data are relatively good estimates of the actual scores evaluated by a judge panel. Error are always lower than 50% except for two samples where a value of 8600 OU/m^3 instead of 4200 OU/m^3 (100% error) and 10 900 OU/m^3 instead of 6700 OU/m^3 (65%) error is obtained. Cross validation should exclude the possibility of wrong models and the results clearly indicate that it is possible to reliably predict odour concentration only from PTR-MS data.

4. Conclusions

In this study we used proton transfer reaction-mass spectrometry, to our knowledge for the first time, to address problems related to the monitoring of composting plants and, in general, to odour control. We have obtained two major results: (i) differences between air collected before and after a biofilter are evident and can be reliably measured indicating possible markers of biofilter efficiency and the possibility of its continuous in situ control and (ii) strong correlation among many PTR-MS spectral line intensities and odour concentration as measured by olfactometric techniques is evident and a proper data analysis based on multivariate calibration can predict olfactive intensity of unknown samples based only on

instrumental PTR-MS data. The agreement of PTR-MS based prediction and actual olfactometric measurements is comparable with the reported uncertainty of this sensorial method. We do not believe that PTR-MS can replace completely the use of olfactometry because, up to now, no model can predict the human response to olfactive stimuli. Our goal is, on the contrary, to show that its rapid and sensitive response and the possibility of accurate calibration with olfactometry makes PTR-MS a powerful and innovative tool for monitoring composting plants and, in general, a useful reference for studies in odour control. In the presence of more experimental data, a better approach should consider a preliminary classification of samples based on some multivariate discriminant analysis (identification of the kind of odour, e.g., composting plant versus farm emissions) followed by the development of different calibration models on the identified clusters.

PTR-MS does not allow, in general, compound separation and many compounds contribute to the observed intensity of every spectrometric peak. Nevertheless, as shown in other studies, it turned out also here that the spectral fingerprint rapidly obtainable by PTR-MS coupled with multivariate analysis of the data can efficiently be used both for classification and for calibration. This is an important technological result because it allows a rapid and systematic pre-screening reducing the use of olfactometric techniques to few critical samples or to the calibration phase.

Odour related issues are among the primary concerns of the public against the implementation of new composting or waste treatment facilities and only an accurate and reliable quantification of odour concentration can warrant both the public welfare and the necessity of waste disposal. Our data indicate that PTR-MS can play an important role by monitoring composting plants and by providing reliable on-line estimation of odour concentration.

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