Talanta 128 (2014) 268–272

Contents lists available at ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

A study on the applicability of zinc acetate impregnated silica substrate in the collection of hydrogen sulfide by active sampling

Oriana Motta [b], Raffaele Cucciniello [a], Claudio Scicali [c], Antonio Proto [a,*]

[a] Department of Chemistry and Biology, University of Salerno, via Giovanni Paolo II 132, 84084 Fisciano (SA), Italy
[b] Department of Educational Philosophic and Human Science, University of Salerno, via Giovanni Paolo II 132, 84084 Fisciano (SA), Italy
[c] Sicilian Laboratory of Analytical and Environmental Consulting, via Matilde Serao 15/A, 95037 San Giovanni La Punta (CT), Italy

ARTICLE INFO

Article history:
Received 10 February 2014
Received in revised form
9 April 2014
Accepted 15 April 2014
Available online 14 May 2014

Keywords:
Hydrogen sulfide
Air sampling
Ion chromatography
Zinc acetate
Biogas

ABSTRACT

A novel substrate for the hydrogen sulfide determination in air was developed based on zinc acetate impregnated silica in glass tubes. Collected H_2S is quantified by ion chromatography after sulfide oxidation to sulfate in an alkaline solution of H_2O_2.

Laboratory tests were conducted in controlled atmosphere to evaluate uptake rate, linearity, sample stability, influence of relative humidity and interfering gases.

A pilot study was also conducted in the field in order to assess the applicability of the substrate and to understand the effect that gases such NO_2 and CH_4 can have on the efficiency of collection of H_2S.

The new substrate has shown to have several advantages with respect to the charcoal substrate, that is the one of choice as reported by National Institute of Occupational Safety and Health (NIOSH) method. In particular it does not suffer from sulfur background and it is not influenced by interfering gases such as NO_2 and CH_4.

1. Introduction

Hydrogen sulfide is an undesirable air pollutant because of its malodor and toxicity even at low concentrations. Concern about health effects is mostly related to the brain and central nervous system, the risk of damage depends on both the exposure time and the concentration of H_2S [1–3].

H_2S has adverse effects also on metals and lead-based pigments where H_2S reacts quickly to form black galena (PbS) [4] and contributes to the formation of acid rain when it is oxidized to SO_2 and/or SO_3.

Due to these concerns considerable attention has been paid on the quantification of ambient H_2S and a number of methods have been developed to achieve widespread routine use [5–8].

The accepted standard method for environmental H_2S determination involves collection of H_2S on $Cd(OH)_2$ suspension followed by reaction with p-amino-N,N-dimethylaniline to produce the dye methylene blue which is then evaluated colorimetrically [9].

Although the method shows high sensitivity and specificity, its convenience is limited by laborious laboratory practice that makes the method inconvenient for field work. Moreover an important aspect to be considered is the instability of the solution of p-amino-N,N-dimethylaniline with ferric chloride that must be prepared fresh each time.

Several alternative methods have been proposed in the past, based on silver–gelatin complex, impregnated paper tape methods by using lead acetate, mercuric chloride, silver nitrate, dicyanoargentato (I), etc. followed by optical densitometric determination of the metal sulfide formed [10–12]. Most of these methods, however, have several weaknesses and limitations including that the impregnated filters are only stable for few months and they are not suitable for sub-ppb H_2S determinations [13].

More recently Occupational Safety & Health Administration (OSHA) [14] used a modified version of NIOSH 6013 [15] that uses shell charcoal to collect hydrogen sulfide. In the laboratory the charcoal is placed in a solution of ammonium hydroxide and hydrogen peroxide that converts the hydrogen sulfide to sulfate. The sulfate is then analyzed by ion chromatography. This medium, however, collects sulfur dioxide which is a positive interference, equivalent to H_2S by approximately twice the SO_2 concentration by weight. Moreover the charcoal, depending on lot, can also suffer from high sulfur backgrounds and poor desorption efficiencies and therefore needs to be treated to high temperature before utilization. In our laboratory experience by heating 500 g of coconut charcoal in a tubular oven at 600 °C for 3 days, under a nitrogen flux, reduces the initial amount of sulfur by 80%.

In addition to the classical active sampling techniques in the last years several substrates have been developed for diffusive (or passive) sampling [13,16–21]. In particular a zinc acetate

---

* Corresponding author Tel.: +39 89969581.
E-mail address: aproto@unisa.it (A. Proto).

http://dx.doi.org/10.1016/j.talanta.2014.04.031
0039-9140/© 2014 Elsevier B.V. All rights reserved.

impregnated silica substrate was successfully employed for the passive sampling of hydrogen sulfide [21] followed by chromatographic analysis of the sulfate produced by the oxidation of sulfide in H_2O_2/NH_4OH solution.

In this work we report a study on the applicability of zinc acetate impregnated silica substrate in glass tubes for active sampling. Tests were conducted under controlled laboratory conditions and in the field during an initial pilot study. Environmental tests were performed in a common waste dump where the sorbent tubes, filled respectively with zinc acetate impregnated silica gel and coconut shell charcoal were exposed concurrently. The advantages of the method are efficient collection of H_2S ($>90\%$), elevated stability and a high selectivity. Moreover it does not suffer from the presence of sulfur in the substrate. Another objective of the pilot study was to understand the effect that gases such NO_2 and CH_4 might have on the efficiency of collection of H_2S. Therefore in order to determine the potential interference of these gases on the collection of H_2S, sampling were conducted in a post combustion plant of a biogas engine generator, where NO_2 was predominant among the other compounds and on the biogas produced by the anaerobic treatment of urban wastes in landfill, where methane was the major component.

2. Experimental

2.1. Preparation of substrate

The substrate was prepared by wet impregnation. Silica gel 18–35 mesh (Macherey-Nagel, Kieselgel 60) was used as the support. Silica gel was previously purified from anions by boiling in Na_2CO_3 solution (1.0 M) for 2 h, washed with distilled water up to pH=7 than dried at 70 °C for 12 h. In a single-neck flask equipped with a magnetic stirrer, 50.0 g of purified silica gel were immersed into an aqueous solution of zinc acetate 0.01 M, prepared dissolving 0.6 g of zinc acetate dihydrate [$Zn(CH_3COO)_2 \cdot 2H_2O$, Reagent grade, Sigma-Aldrich] in 250 mL of distilled water for 1 h at room temperature. Water was removed using rotary evaporator in order to obtain a substrate composition being 1% wt in zinc acetate. Coconut shell charcoal purchased from Asbury Carbon Inc. was used as reference sorbent as indicated for H_2S measurement in air by active sampling [15]. Charcoal was purified by heating at 600 °C in a tubular oven for 3 days, under a 3 L/min flux of nitrogen.

2.2. H_2S sorption and sulfide oxidation in alkaline solution

H_2S is captured on the substrate forming stable ZnS following the reaction:

$$H_2S+Zn\ (CH_3COO)_2=ZnS+2CH_3COOH$$

S^{2-} oxidation to SO_4^{2-} is successively performed in an alkaline solution prepared mixing 2.0 mL of NH_4OH 0.2 M, 5.0 mL of H_2O_2 30% and 3.0 mL of distilled water for 15 min in an ultrasonic bath at 50 Hz (Falc LBS 1–6 Ultrasonic Instrument, Italy) and room temperature. Stoichiometry of the reaction is

$$S^{2-}+4H_2O_2=SO_4^{2-}+4H_2O$$

By the use of Ultrasonic bath [22] oxidation is completed within 15 min.

To evaluate the oxidation efficiency of the reaction a series of laboratory experiments were conducted. Seven weighed ZnS (Reagent grade, Sigma-Aldrich) samples (ranging between 0.20 and 1.14 mg of sulfide) were placed in as many vials and then oxidated as previously described. After chromatographic analysis, the measured sulfate content was related to the weighed ZnS amount.

2.3. Ion chromatographic quantification of SO_4^{2-}

H_2S was determined as SO_4^{2-}, after extraction, using a Dionex DX 120 ion chromatograph (Dionex, Sunnyvale, CA, USA), equipped with a Ion Pas AS14 column (4 mm × 250 mm). The eluent was 1.8 mM Na_2CO_3:1.6 mM $NaHCO_3$ at a flow rate of 0.8 mL/min and a pressure of 1050 psi. The calibration was performed by injecting 20 μL of five standard SO_4^{2-} solutions in the range 1–10 μg/mL. All the reagents were reagent grade purchased from Sigma-Aldrich.

2.4. Sorbent tube preparation for H_2S capture

Two-bed sorbent tubes were prepared introducing 0.8 g and 0.2 g of zinc acetate impregnated silica gel, divided by a porous unreactive polyethylene septum, into a glass tube 10 cm long and with an internal diameter of 6.0 mm. The smallest septum was employed to evaluate a possible saturation of the septum directly exposed to the monitored environment. The front end of this tubular device was connected to a pump AP Buck VSS 1 (Aquaria srl, Italy) while the other end was exposed to the monitored environment. Laboratory tests were conducted under controlled concentrations of H_2S, humidity and sampling flow rate to evaluate the reliability of the novel device.

2.5. Field sampling and evaluation of interferences

A pilot study was conducted in the field: environmental sampling was performed in a common waste dump where the sorbent tubes, filled respectively with zinc acetate impregnated silica gel and coconut shell charcoal (Aquaria srl, Italy), were exposed concurrently. Another objective of the pilot study, besides the interference of SO_2, was to understand the possible interference of gases such as NO_2 and CH_4. SO_2 and NO_2 were sampled using a bubbler at a flow rate of 0.5 L/min, equipped with an oxidant solution of $KMnO_4$ 0.025 M and NaOH 1.25 M, then analyzed chromatographically as sulfate and nitrate, whereas CH_4 was measured using an IR detector (Biogas Check, Geotechnical Instruments UK Ltd.). Measurement accuracy was assessed by comparison with reference method as reported by NIOSH (NIOSH 6013). The flow rate of the sampling was maintained at 0.5 L/min exposing each sorbent tube for 1 h. After the sampling, samples were stored at room temperature before analysis.

3. Results

3.1. Sorbent tube sorption efficiency determination

Efficiency of collection was determined as a function of H_2S concentration, flow rate, sampling time and humidity, under controlled atmosphere in a chamber equipped with an humidity controller on both charcoal and zinc acetate impregnated silica substrates. All measurements were made at room temperature ($T=25\pm1$ °C) and atmospheric pressure. Relative humidity was varied from 1 to 75%, sampling time was set to 1 and 4 h at a flow rate of 0.5 L/min and to 1 h at flow rates of 0.5 and 1.5 L/min, while the H_2S concentration was kept constant at 70 ppb for the convenience of analysis. Results are reported in Table 1. It can be observed that, within the range of conditions studied, the efficiency is not affected by flow rate, humidity and sampling time being always $>97\%$ for both the substrates used for the collection of H_2S.

Table 1
Efficiency of H_2S collection ($T=25$ °C, $H_2S=70$ ppb).

Substrate	Flow rate (0.5 L/min)	Flow rate (1.5 L/min)	Sampling time (1 h)	Sampling time (4 h)
Charcoal	99 ± 2%	98 ± 2%	–	N.D
Zinc acetate	98 ± 3%	97 ± 2%	–	N.D
Charcoal	–	N.D	99 ± 2%	100 ± 1%
Zinc acetate	–	N.D	100 ± 1%	99 ± 2%

N.D. means that in these conditions of flow rate and sampling time measurements were not accomplished

Table 2
Recovery of hydrogen sulfide after oxidation with H_2O_2/NH_4OH.

	Recovery of hydrogen sulfide as sulfate						
Sulfide amount (mg)	0.20	0.33	0.37	0.44	0.60	0.85	1.14
Recovery (%)	100 ± 2	100 ± 1	99 ± 2	98 ± 1	100 ± 1	100 ± 3	99 ± 2

3.2. Reproducibility, detection limit and storage

Quantitative determination of sulfide, sorbed on zinc acetate impregnated silica substrate, was made by the chromatographic measurement of the sulfate formed after oxidation in a H_2O_2/NH_4OH solution. To test the applicability of this method in a wide range on concentrations, a dedicated study was developed in laboratory. A series of weighed samples of ZnS (Reagent Grade, Sigma-Aldrich) were dissolved in the alkaline and oxidant solution and then analyzed by ion chromatography. The sulfate measured was compared to the previously weighed zinc sulfide and, as shown in Table 2, a complete conversion is always observed.

According to EN 13528-2 the limit of detection (LOD) is expressed as three times the standard deviation of the blank values. The calculated LOD value, considering a 1 h sampling period at 25 °C, was 5 ppb. Precision is estimated from 2σ deviation of the absolute differences of the individual sample values to the mean of the triplicate samples. Replicate precision was evaluated to be 0.4% of the mean in all cases.

Chromatographic analyses were repeated three times in order to test the reproducibility of the instrument and a set of three unexposed samples were analyzed to determine the blank values. Moreover, in order to evaluate the effect of storage time before analysis a set of three unexposed sorbent tubes, prepared as previously described, were stored at room temperature for six weeks and then analyzed. Results showed no changes in the blank value even after storage.

3.3. SO_2, NO_2 and CH_4 interference

Sulfur dioxide represents a positive interference in H_2S measurements using charcoal as a sorbent for sampling, as reported in NIOSH method 6013 [15]. In order to evaluate the influence of SO_2 on hydrogen sulfide capture and determination, two series of three sorbent tubes, filled respectively with charcoal and zinc acetate impregnated silica, were concurrently exposed to 500 $\mu g/m^3$ of SO_2 for 1 h at a flow rate of 0.5 L/min. Results showed that SO_2 was only lightly (8%) adsorbed on zinc acetate substrates, whereas an extensive adsorption (85%) was found using activated charcoal, in accordance to what reported in the literature [23]. This is an advantage that can be underlined when choosing zinc acetate as substrate for the H_2S determination.

The effects of NO_2 and methane on the determinations of H_2S were also evaluated in a series of laboratory experiments, as follows: five sorbent tubes loaded with zinc acetate on silica and five loaded with charcoal were exposed to 20 mg/m^3 of H_2S and respectively to 500 mg/m^3 of NO_2 and 50%(v/v) of methane, for one hour at a flow rate of 0.5 L/min, in order to reproduce the environmental conditions of the ambient monitored during the field evaluation. It was revealed that NO_2 and methane have a significant effect on H_2S sampled on charcoal allowing to an underestimation of the H_2S. In particular, NO_2 caused a 20 ± 2% (average ± standard deviation on five trials) interference while methane caused a 10 ± 1% interference. This trend was also observed in the field experiments as reported below. No measureable interferences were observed when zinc acetate impregnated silica substrate was employed. This is a further advantage of our substrate with respect to activated charcoal.

3.4. Field sampling

Fig. 1 reports data obtained in the field by monitoring H_2S in a in a common waste dump where charcoal filled glass tubes are concurrently used with zinc acetate impregnated silica glass tubes.

Results show a good correlation between H_2S concentration measured respectively after sorption on charcoal and zinc acetate sorbents. Pearson's correlation coefficient is 0.98; all the model parameters are significant at a 99% confidence level ($p<0.001$).

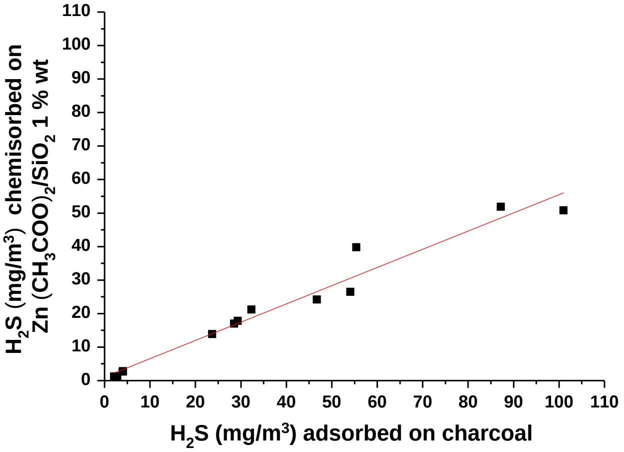

Fig. 1. Comparison of H_2S concentration obtained by using charcoal and zinc acetate impregnated silica substrates .

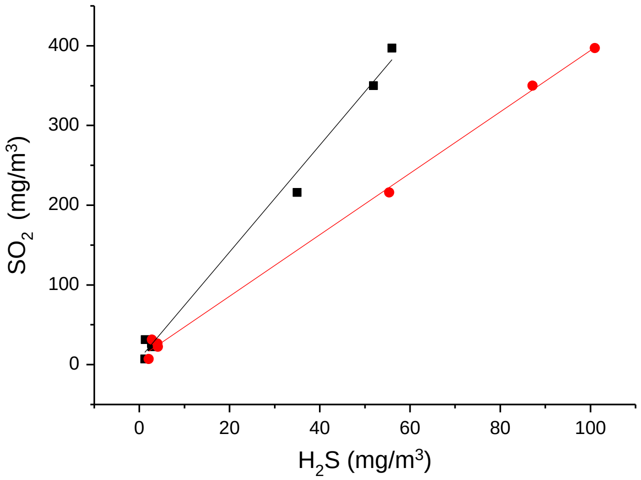

Fig. 2. Influence of SO_2 concentration on H_2S determination with charcoal (●) and zinc acetate impregnated silica sorbents (■).

Table 3
NO_2, CH_4 and SO_2 effects on H_2S determination in the monitored sites.

Sample	Volume sampled (L)	H_2S (mg/Nm^3) Charcoal	H_2S (mg/Nm^3) Zinc acetate on silica	SO_2 (mg/Nm^3)	NO_2 (mg/Nm^3)	CH_4 (%)
Combusted biogas 1	29.8	47.1 ± 0.5	117.6 ± 12.0	3.1 ± 0,03	424 ± 4	0.1 ± 0.001
Combusted biogas 2	27.9	81 ± 0.8	98.6 ± 10.0	12 ± 0.1	1314 ± 13	0.1 ± 0.001
Combusted biogas 3	29.8	16.8 ± 0.2	100.2 ± 10.0	7 ± 0.07	558 ± 6	0.1 ± 0.001
Biogas 1	28.8	61.1 ± 0.6	125.6 ± 12.6	142 ± 14	35 ± 0.4	48.4 ± 0.5
Biogas 2	28.9	125.8 ± 13	149.6 ± 15.0	191 ± 19	6.2 ± 0.06	49.7 ± 0.5

It can be easily observed that H_2S concentration measured using charcoal is approximately twice the value obtained by using zinc acetate. This was an expected result considering that in the monitored sites SO_2 was predominant respect to H_2S and significantly affected values obtained with charcoal sorbent tubes that, as also reported in the NIOSH method [15], was overestimated.

During this monitoring program SO_2 was measured using a bubbler to trap it, followed by chromatographic determination of sulfate. Fig. 2 reports a graphic where the value of the measured SO_2 is correlated to the measured H_2S concentration.

It can be observed that the curves present different slopes, the one relative to charcoal being lower compared to that of zinc acetate impregnated silica.

SO_2 influences the adsorption capacity of H_2S also on silica substrate, due to its high superficial area, but the effect is much more limited with respect to charcoal substrate. On this latter a chemical reaction occured on the activated carbon surface, as reported by Zhang et al. [23]. They stated that the load capacity of activated carbon is much greater than for normal physical adsorption, due to the chemical reaction, and that the chemical form of SO_2 on the carbon is likely to be H_2SO_4. A possible reaction mechanism, catalyzed by carbon, was proposed as follows [23]:

$$SO_{2\ ads}+1/2O_{2\ ads}\rightarrow SO_{3\ ads} \tag{1}$$

$$SO_{3\ ads}+H_2O_{\ ads}\rightarrow H_2SO_{4\ ads} \tag{2}$$

The SO_2 loading potential of activated carbon increases with increasing the concentration of SO_2 in the air. This effect has its reason in the fact that with increasing SO_2 concentration the chemical reaction rate increases relative to pure adsorption rate.

Our results are in great agreement to what reported by Zhang et al. [23]. Fig. 2 reveals that the interference of SO_2 enhances with its increasing concentration and this effect is much more pronounced on charcoal substrate. These results are strictly linked to those obtained in the laboratory tests, described above, where we found a very light SO_2 adsorption using zinc acetate on silica (8%) with respect to charcoal (85%).

Another objective of the pilot study was to understand the effect that gases such as CH_4 and NO_2 might have on the efficiency of collection of H_2S. Therefore sampling was conducted on biogas produced by the anaerobic treatment of urban wastes in landfill, where methane is the major component and at the end of a catalytic thermo reactor, for the conversion of CO and CH_4 in CO_2, in a post combustion plant of a biogas engine generator, where NO_2 was predominant among the other compounds. Results of H_2S concentration measured by both substrates are reported in Table 3 together with the concentrations of NO_2 and CH_4. It can be observed that H_2S is underestimated due to the presence of the other gases when charcoal is used as substrate. Interestingly we can note that when SO_2 is also present in high concentration (as in the case of the landfill where biogas is produced) the difference between values obtained by both substrates becomes smaller.

4. Conclusion

This work shows that zinc acetate impregnated silica sorbent is a favorable alternative to charcoal for the active collection of hydrogen sulfide. The proposed substrate is easy to prepare, stable after preparation and does not require high temperature for purification. On the contrary charcoal needs to be treated at 600 °C in order to reduce sulfur that interferes with the measure of H_2S. Precision, LOD and storage conditions were analyzed and all met the requirements of the official method reported by NIOSH.

The substrate was tested in a series of laboratory experiments and successfully utilized for the determination of H_2S in ambient air. In the presence of interfering gases such as SO_2, NO_2 and CH_4, it showed to be much less influenced with respect to charcoal thus avoiding over- and underestimation.

Conflicts of interest

The authors declare no conflict of interest.

Acknowledgments

This work was financially supported by Fondi di Ateneo per la Ricerca di Base (FARB 2012), University of Salerno. Authors are indebted with Aquaria Research srl for providing carbon tubes and with Dott.ssa Rosa La Femina and Dott.ssa Francesca Esposito for technical assistance.

References

[1] Health Assessment Document for Hydrogen Sulfide, (1986). EPA/600/8–86/026, US Environmental Protection Agency, Washington, DC.
[2] Legator M.S., Singleton C., 1997. Panel on hydrogen sulfide. American Public Health Association's annual meeting, Nov. 11, Indianapolis, IN.
[3] B. Tvedt, K. Skyberg, O. Aaserud, A. Hobbesland, T. Mathiesen, Am. J. Ind. Med. 20 (1) (1991) 91–101.
[4] G.D. Smith, R.J.H. Clark, J. Cult. Herit. 3 (2002) 101–105.
[5] R.M. Bethea, J. Air Pollu. Cont. Assoc. 23 (8) (1973) 710–713, http://dx.doi.org/10.1080/00022470.1973.10469832.
[6] B. Morris, M. Jacobs, M. Braverman, S. Hochheiser, Anal. Chem. 29 (9) (1957) 1349–1351, http://dx.doi.org/10.1021/ac60129a028.
[7] R. La Rue, O.Y. Ataman, D.P. Hautman, G. Gerhardt, H. Zimmer, H.B. Mark Jr., Anal. Chem. 59 (19) (1987) 2313–2316.
[8] R.S. Braman, J.M. Ammons, J.L. Bricker, Anal. Chem. 50 (7) (1978) 992–996, http://dx.doi.org/10.1021/ac50029a041.
[9] M.B. Jacobs, J. Air Pollu. Cont. Assoc. 15 (7) (1965) 314–315, http://dx.doi.org/10.1080/00022470.1965.10468385.
[10] D.F.S. Natusch, J.R. Sewell, R.L. Tanner, Anal. Chem. 46 (3) (1974) 410–415.
[11] E.T. Hayes, O.Y. Ataman, A.E. Karagozler, Y.L. Zhang, D.P. Hautman, R. T. Emerich, A.G. Ataman, H. Zimmer, H.B. Mark Jr., Microchem. J. 41 (1990) 98–105.
[12] A.E. Eroğlu, M. Volkan, E. Bayramh, O.Y. Ataman, H.B. Mark Jr., Fresenius J. Anal. Chem. 355 (1996) 667–671.
[13] F. De Santis, I. Allegrini, R. Bellagotti, F. Vichi, D. Zona, Anal. Bioanal. Chem. 384 (2006) 897–901.
[14] Occupational Safety &Health Administration (2006). Sampling and Analytical Methods: Hydrogen Sulfide. OSHA. 200 Consitution Ave, NW, Washington, DC 20210.

[15] Cassinelli M.E. (1994) Manual of Analytical Methods (NMAM). Hydrogen Sulfide: method 6013, issue 1, National Institute of Occupational Safety and Health (NIOSH) Cincinnati, OH.

[16] R. Cucciniello, A. Proto, D. Alfano, O. Motta, Atmos. Environ. 60 (2012) 82–87.

[17] R. Cucciniello, A. Proto, F. Rossi, O. Motta, Atmos. Environ. 79 (2013) 666–671.

[18] A. Proto, R. Cucciniello, F. Rossi, O. Motta, Environ. Sci. Pollut. Res. 21 (2014) 3182–3186, http://dx.doi.org/10.1007/s11356-013-2369-3.

[19] H.A. Ankersmit, N.H. Tennent, S.F. Watts, Environment 39 (2005) 695–707.

[20] F. De Santis, T. Dogeroglu, A. Fino, S. Menichelli, C. Bazzana, I. Allegrini, Anal. Bioanal. Chem. 373 (2002) 901–907.

[21] Aquaria srl, Instruction manual for Ring Sampler, 〈http://www.aquariasrl.com〉.

[22] A. Kotronarou, G. Mills, M.R. Hoffmann, Environ. Sci. Technol. 26 (12) (1992) 2420–2428.

[23] P. Zhang, H. Wanko, J. Ulrich, Chem. Eng. Technol. *30* (5) (2007) 635–641.