

ASSESSMENT OF SOME ORGANIC POLLUTANTS FROM COMBUSTION PROCESSES. PRELIMINARY RESULTS OF LABORATORY AND FIELD TESTS.

Maspero M.⁽¹⁾, Rusconi M.⁽¹⁾, Fiore A.⁽²⁾, Negri A.⁽¹⁾, Sanavio D.⁽²⁾

(1) CESI Spa, Environment Business Unit

(2) ENEL Produzione Spa, Piacenza Laboratory

Abstract

Italian Law on emission limitation and control requires 54 organic compounds to be determined in the flue gases of industrial combustion plants. These compounds show very different chemical and physical characteristics (e.g. volatility, stability, reactivity with water ...). Some of these compounds (i.e. PAH, PCDD/PCDF, VOC) are commonly monitored in emissions of Large Combustion Plants, but for the majority of them a validated standard method doesn't exist, neither at Italian nor at international level.

A preliminary laboratory investigation has therefore been performed, which allowed to focus on the most promising methods for some of the above mentioned compounds. During this phase, US-EPA, OSHA and NIOSH methods, together with the technical literature, have been reviewed and some tests have been performed on a small scale test rig.

The selected methods have then been field tested on a low-sulfur heavy fuel oil fired power plant, equipped with ESP and SCR, and on a coal-fired power plant, equipped with ESP, FGD and SCR (the results of this last test are only partially accounted for in this paper, because lab analyses are still in progress).

Experimental tests performed allowed to select and verify –at least in a preliminary way- a series of procedures suitable for the sampling in combustion flue gases of about 30 organic pollutants.

1 INTRODUCTION

Italian Law on emission limitation and control (Environment Ministry Decree N.51 of July 12, 1990) requires 54 organic compounds -defined as “carcinogenic, mutagenic or highly toxic”- to be determined in the flue gases of industrial combustion plants. These compounds show very different chemical and physical characteristics (e.g. volatility, stability, reactivity with water ...). Some of these compounds (i.e. PAH, PCDD/PCDF, VOC as Total Organic Carbon) are commonly monitored in power plants and others Large Combustion Plants (LCP) emissions, but for the majority of them a standard method -validated for combustion flue gases- doesn't exist, neither at Italian nor at international level [*Bertolaccini 1991, Johnson 1988, Wagoner 1991*].

ENEL Produzione planned and financed a comprehensive R&D program, developed and carried out by CESI during 1999 and 2000, aimed to the development and testing of sampling and analysis methods for some of the above mentioned compounds. The following compounds have been excluded:

- Polycyclic Aromatic Hydrocarbons (PAH), Dioxins and Furans (PCDD and PCDF), Polychlorobiphenyls (PCB) because Italian (i.e. UNICHIM Method N.825) and/or international (i.e. ISO/DIS 11338 and EN1948) methods were already available or in the development stage;
- 1-methyl-3-nitro-1-nitrosoguanidine and methyl-ONN-azosymethylacetate because of their very high reactivity, that will make sampling impossible or very difficult,
- propylenimine because of its commercial unavailability.

The first step of the program has been a grouping of the remaining 36 compounds (see Table 1) according to their chemical and physical characteristics and to the preliminary definition of the potentially suitable methods. The results are summarized in Table 2. During this phase, US-EPA, OSHA and NIOSH methods, together with the technical literature, have been reviewed.

Following steps have been:

- laboratory development and tuning of the analytical instrumental techniques,
- laboratory test of the recovery rates from liquid or solid sampling supports,
- test of sampling methods, by means of a small scale test rig,
- field test of the selected sampling methods, on a low-sulfur heavy fuel oil fired power plant, equipped with ESP and SCR, and a coal fired Power Plant equipped with SCR, ESP, FGD.

2 MATERIALS AND METHODS

2.1 Method testing at a laboratory scale

The different sampling systems have been tested on a small scale test rig composed of: inlet air filter; heating coil, housed into a suitable temperature controlled oven; water injection system; VOC dynamic spiking system; gas cylinders as sources of NO_x, SO₂; glass gas mixing device; support for the various sampling trains tested; sampling system, with suction pump, temperature and flow rate metering/recording system.

With this rig it has been possible to generate a simulated exhaust flow, at a temperature between 120 and 200 °C and with composition roughly similar to combustion effluents (i.e. 10% vol. humidity, 600 mg/m³ SO₂, 200 mg/m³ NO_x).

2.2 Field tests

Field tests have been performed a low-sulfur heavy oil fired power plant, equipped with ESP and SCR. Sampling have been performed at the stack (80 meters from the ground). During the last quarter of 2000, a second field test has been performed on a coal-fired power plant, equipped with ESP, FGD and SCR. The results of this last test are partially accounted for in this paper, because laboratory analyses are still in progress. In both cases sampling was performed downstream of all pollution control plants.

To reduce the length of field test, instead of dynamic spiking, requested by US-EPA Method N.301 [US-EPA 1987], sampling solid adsorbents and filters and liquid adsorption solutions have been spiked, at the laboratory or directly on-site, with the desired target compounds, in methanol or methylene chloride solutions. To evaluate method suitability, the criteria recommended by US-EPA has been used, i.e. the recovery percentage of the spiked compounds had to lie between 70 and 130%, with a relative standard deviation (RSD) less than 50%. For the semi-volatile compounds, sampled with US-EPA Method N.0010 train [US-EPA 1986a], the acceptability criteria used implied recovery rate between 50 and 150%, with standard deviation less than 50%. Methods with lower recovery percentage, but with very low standard deviation (i.e. less than 20%), have been accepted too: in this case, in fact, a correction factor, based on the recovery efficiency, can be applied to the results.

2.3 Sampling methods

The main information about the sampling methods used are summarized here below. At the end of each sampling, all samples were stored at 4°C before analysis.

Sampling with KOH solutions. N,N'-dimethylnitrosoamine and hexamethylphosphoramide was sampled by bubbling flue gases into basic solutions [Rounbehler 1980]. The sampling train was composed of: sampling probe without dust filtration, four washing bottles (with sintered frit) in series, each with 50 mL of KOH 0,1 N, immersed into a refrigerated bath (maintained at -10 to -20 °C), suction pump and flow rate metering/regulating devices. Sampling flow rate has been maintained at 2 L/min, until about 100 L was sampled. At the end of each sampling, the probe has been washed with KOH 1N and the washing solution has been stored for the analysis.

Sampling with sulfuric acid treated filters. This method, derived from OSHA Methods N. 65, 71 and 93 [OSHA 1989a,b, 1992a], has been used for: 2-naphthylamine, 3,3'- dimethoxybenzidine, 3,3'-dichlorobenzidine, 3,3'-dimethylbenzidine, 4,4'-methylenebis(2-chloroaniline), 4-aminobiphenyl and benzidine. For samplings, two 47 mm glass fiber filters (Gelman A/E) impregnated with sulfuric acid have been used, housed into a suitable filter holder with PTFE spacers. 10 L of flue gases have been sampled at a flow rate of 1 L/min, in non-isokinetic conditions. All filters have been stored into a 10 mL glass vial, already containing 2 mL of deionized water.

Sampling with Tenax. Tenax has been used for dimethylsulfate and diethylsulfate. Sampling has been performed using glass tubes (external diameter 6 mm, length 100 mm), filled with Tenax TA (Supelco) and suitable for Dynatherm thermal desorber. Flow rate was around 0,3 L/min, for a total sampled volume of 4 - 5 L of non filtered flue gases. All tubes vials have been stored in Teflon container accurately sealed.

Sampling with active charcoal traps. This method, derived from UNI 10493 [UNI 1996], has been used for 1-chloro-2,3-epoxypropane (epichlorohydrin), 1,2-epoxypropane (propylene oxide), 1,2-dichloroethane, 1,3-dichloro-2-propanol. Because of the high water solubility of the first three species, sampling has been performed by means of a dilution probe, with a maximum ratio of 1:10 between flue gases and dilution gas (chromatographic nitrogen). A two-section charcoal tube (800/200 mg) has been used, with sampling flow rate of 1 L/min and a total sampled volume of 50 L maximum (i.e. 5 L flue gases).

Sampling with HCl 0,1 N solution. This procedure, derived from NIOSH Methods N.3503 and 3515 [NIOSH 1994a,b], has been used for N,N'-dimethylhydrazine and hydrazine. The sampling train includes two washing bottles, with sintered frit, in series, filled with 50 mL of HCl 0,1 N solution, inserted into a refrigerated bath. With a flow rate of 1 L/min, around 50 L of exhaust gases have been sampled. At the end of the sampling, the probe has been washed with the HCl 0,1 N solution that has been stored for analysis.

Sampling with water. Sampling of ethylenethiourea has been performed by flue gases bubbling into four washing bottles with sintered glass frit, filled the first with 10 mL and the others with 40 mL of deionized water, and kept just above 0 °C with the aid of a refrigerated bath. Sampling flow rate has been 2 L/min with a total sampled volume of 100 L maximum. The probe has been washed with deionized water.

Sampling with filters and solid adsorbent (XAD-2 resin). This method, derived from US-EPA SW-846 Method 0010 [US-EPA1986a] has been used for PCB, PCT, sulfallate, 1,2-dibromoethane, 2-nitropropane and 1,3-propane sultone. The sampling train, in the version realized by CESI, is composed of: stainless steel probe, with S-type Pitot tube and thermocouple, glass fiber thimble filter holder, borosilicate glass flue gases refrigeration/condensation system, first glass vial filled with 30 g XAD-2 resin, condensate collection tank, second glass vial again with 30 g XAD-2, suction pump, flow rate and temperature metering/regulating devices. Condensate collection device and XAD-2 adsorption areas have been maintained at 17 ± 3 °C during all the samplings. Sampling has been performed isokinetically, at a flow rate of 10 - 15 L/min and with a sampled volume around 2 - 3 m³. The probe and the sampling train have been washed by countercurrent circulating 1 L acetone for at least 20 minutes, by means of a peristaltic pump; the washing has been stored for subsequent analysis.

Sampling with mixed solid adsorbents. This sampling train, realized by CESI according to US-EPA Method 0031 [US-EPA 1996a], has been used for compounds showing boiling point between 30 and 100 °C (in this case: propylene oxide, ethylenimine, chloromethyl(methyl)ether, N-N'-dimethylhydrazine, acrylonitrile, benzene, 1-2dichloroethane, bis-chloromethylether, hydrazine, epichlorhydrin, 2-nitropropane, 1-2dibromoethane, beta-propiolactone, dimethylcarbamoylchloride). The train is composed of: borosilicate glass heated probe, with in-stack dust filter, probe insulating valve, water-cooled condenser, first VOC adsorption trap (1 g Tenax), condensate collection vessel, second VOC adsorption trap (600 mg Tenax and 600 mg activated charcoal), third VOC adsorption trap (1 g Carboxipack and 200 mg Carboxisieve S-III), suction pump and flow rate and temperature metering/regulating devices. All the traps were of suitable dimensions for thermal desorber Dynaterm Acer 900. In case of very reactive or humidity sensitive species, a dilution probe was used, with chromatographic N50 air as diluent (1:10 dilution ratio).

Sampling with Tedlar[®] bags. This method, derived from US-EPA SW-846 Method N.0040 [US-EPA 1996b] has been used for vinyl chloride, 1,3-butadiene, ethylene oxide, propylene oxide, 1,2-dichloroethane and benzene sampling. The sampling train is composed of: dilution probe (with a dilution ratio of 1:10, with N50 chromatographic air as dilution gas), T piece, with regulation valve, 10 L Tedlar bag (SKC), with inlet needle valve. The bag was housed into a suitable container under vacuum. Sampling duration was fixed at 30 minutes. Dilution ratio has been checked by injecting, at the probe inlet, a 100 ppm CO gas mixture, and measuring in/out concentration with a NDIR analyzer.

Sampling with methanol and activated charcoal trap. This method, derived from the US-EPA CTM-008 [US-EPA 1998] has been used for acrylonitrile. Sampling train includes: sampling probe, washing bottle with 25 mL of methanol, kept at 0 °C, activated charcoal trap (two sections: 800/200 mg) and low flow rate suction pump. By this sampling train, 6 L of flue gases have been collected at a flow rate of 50 mL/min.

2.4 Analytical methods

Analytical grade reagents was used; deionized water has been obtained by a Millipore MilliQ system. XAD-2 resins have been purified according to the US-EPA Method 0010, appendix A [US-EPA 1986a]. Solid adsorbents have been purified by thermal desorption at the temperature selected for analyses and checked before use, to verify the absence of the compounds of interest. Standards have been obtained, as pure substances or solvent solutions, by different suppliers (Aldrich, Supelco, ChemService).

Some details about analytical methods used are reported here below. Otherwise indicated, analytes were been identified according to retention time of standard solution of pure compounds and quantitative analysis has been performed by external standard method by means of linear regression calibrations.

N,N'-nitrosodimethylamine and hexamethylphosphotriamide. Adsorption solutions have been extracted with dichloromethane and analyzed by HRGC/FID with confirmation by GC/MS.

2-naphthylamine, 3,3'-dimethoxybenzidine, *3,3'*-dichlorobenzidine, *3,3'*-dimethylbenzidine, *4,4'*-methylenebis(2-chloroaniline), *4-aminobiphenyl, Benzidine*. Filters were extracted with water in the same vials used for storage. Then NaOH and toluene were added to aqueous solution and the vials shaken vigorously. After phase separation, 1 mL of toluene has been transferred into another vial, and the nitrogen compounds have been derivatized by adding 25 μ L of HFAA. After 10 min, 1 mL of buffer solution has been added to destroy excess of derivatization reagent. After phase separation, the solution has been directly injected into a HRGC/ECD with capillary column.

Diethyl sulfate and Dimethyl sulfate. Before analysis by GC/FPD, Tenax tubes have been dried, at room temperature and thermally desorbed. Compounds were then directly transferred into the GC.

Vinyl chloride, 1,3-butadiene and benzene (Tedlar bags). From Tedlar bags used for the samplings, 60 mL of sample has been aspirated, by a gas tight syringe, through a Carbotrap 200 tube (Supelco), suitable for Dynatherm thermal desorber. The tube has been inserted into the desorber and compounds have been desorbed for 10 min at 250 °C into a concentration tube (Carbotrap 201, Supelco). This tube has been thermally desorbed (10 min at 250 °C) directly into the GC/MS column. HRGC/MS (Varian SATURN ion trap) operated in EI, acquiring ions between 38 and 140 amu, in full scan mode. Each compound has been identified by retention time and confirmed by mass spectrum. Quantification was made on a specific ion. Calibration standards have been prepared in Tedlar bags and treated in the same way as the samples.

Epichlorohydrin, propylene oxide, 1,2-dichloroethane, 1,3-dichloro-2-propanol. The two sections of the charcoal traps (800 and 200 mg) have been transferred into separated containers and desorbed. After desorption, the solutions were analyzed by HRGC/FID (Varian 3600).

Hydrazine and N,N'-dimethylhydrazine. From the sampling solution (HCl 0.1 N), two aliquots have been taken for separated colorimetric determination of the two compounds. Hydrazine has been determined as a derived product from reaction with p-dimethylbenzaldehyde; N,N'-dimethylhydrazine by developing the reaction with phosphomolybdic acid. Details of analytical procedure are in NIOSH method N. 3503 and 3515 [NIOSH 1994 a,b].

Ethylenethiourea. Analysis has been performed by directly injecting the condensate (10 μ L) into a HPLC/UV (Spectra Physics), with a C18 column (Supelco). Eluent was water/methanol (90:10 v/v) at a flow rate of 1 mL/min. The UV detector operated at 234 nm.

Sulfallate, 1,2-dibromoethane, 2-nitropropane, 1,3-propane sultone. Compounds have been extracted from the sampling train following the same method used for PCT and PCN (see next paragraph). Analysis has been performed by HRGC/MS (Finnigan TSQ70) with EI at 70 eV.

Polychloroterphenyls (PCT). PCT have been extracted from the US-EPA Method 0010 sampling train according to EPA method 3542 [US-EPA 1986b]. Thimble filters and XAD-2 cartridges have been extracted in Soxhlet for 24 hours, with dichloromethane. Acetone, used for train washing, and condensate have also been extracted and concentrated. The analysis has been made by HRGC/ECD (Carlo Erba 5300). For calibration a commercial PCT solution (Aroclor 5460) has been used. Quantitative determination has been made with the external standard method, using the total area of the commercial solution; PCT presence has been confirmed by GC/MS.

Polychloronaphtalenes (PCN). Extraction procedure was the same used for PCT. Extracts have been concentrated and analyzed by HRGC/MS-SIM (Finnigan TSQ70) with EI at 70 eV. For each PCN class two ions of molecular cluster have been acquired. PCN quantification has been made according to the Heidemann procedure [Heidemann 1988], which uses a reduced number of PCN congeners in order to obtain an average response factor for the eight classes. The solution for response factor calculation contained 1,4-dichloronaphtalene, 2,7-dichloronaphtalene, 1,5-dichloronaphtalene, 2,3-dichloronaphtalene, 1,2-dichloronaphtalene, 1,8-dichloronaphtalene, 1,2,3,4-tetrachloronaphtalene and octachloronaphtalene, each of them at a concentration of about 10 μ g/mL in methylene chloride. Average response factors (ARF) for each of those PCN has been computed from ten repeated injections of this solution. ARF obtained have been normalized to that of 1,2,3,4-tetrachloronaphtalene and a regression line between response factor and degree of chlorination has been computed. From the parameters of this regression, the response factors for the chlorination classes of

the PCN for which the standard was not available (i.e. those with 3, 5,6 and 7 Chlorine atoms) have been derived. Tests have been performed with different Halowax solutions, showing errors of $\pm 15\%$ of the nominal PCN concentration.

Acrylonitrile. Methanol has been analyzed directly, while activated charcoal traps have been desorbed (1 hour with 4 mL methanol with 2% formic acid). Solutions have been analyzed by HRGC/NPD.

3 Results and discussion

N-N'-nitrosodimethylamine (NDMA). Three different sampling methods have been tested for NDMA, i.e. KOH 1 N solution, Thermosorb/N trap and Tenax. The last two methods have been demonstrated inadequate, during field test, due to the almost total loss of NDMA added to the sampling supports. Satisfactory results, have been obtained with KOH solutions, both in the laboratory simulations and on site. Special care must be given during concentration of the methylene chloride solutions, avoiding the complete drying, because in this case irreversible losses of NDMA can occur. Laboratory extraction tests from 50 mL NaOH solutions, spiked with 10-100 μg of NDMA, have shown percent recovery rates between 78 ± 4 (100 μg , n=3) and 88 ± 3 (10 μg , n=3). Storage tests of basic solutions, spiked with NDMA, have shown at least a 10 days stability.

Sampling method has been verified during simulated lab tests, with an exhaust gases sampled volume of about 100 L: a recovery rate of $79\pm 6\%$ has been obtained, when spiking the first washing bottle with 10-100 μg of NDMA. The compound was found over the first two bottles. Better results are obtained by keeping the washing bottles around 0 °C. By injecting the NDMA through the heated sampling line, a recovery greater than 80% has been obtained, with NDMA distributed over all the three bottles. Therefore, a set of four washing bottles has deemed necessary for field sampling.

Field tests (three replicated samples) have been performed by spiking the first washing bottle with 10 μg of NDMA: a recovery of $70\pm 2\%$ has been obtained. During the tests, the possible artifact formation (reaction of dimethylamine with nitrogen oxides) has been investigated, by spiking the first bottle with 100 ng of DMA and analyzing the solutions: NDMA has never been found (D.L.= 0.3 mg/L).

Hexamethylphosphotriamide. This is a semi volatile, water soluble, compound, which reacts with strong oxidants and acids. Due to this fact, the sampling with US-EPA 0010 Method has given ambiguous results [Johnson 1999, Radian Corporation 1991, Wagoner 1991], probably because degradation during exhaust gases humidity condensation. Therefore, a sampling in basic liquid solutions has been preferred, in order to minimize possible reactions with acids.

Also lab and field recovery rates of US-EPA 0010 train have been tested. First of all, the recovery percentage of hexamethylphosphotriamide from different sampling supports has been tested: from filters the recovery is quantitative (more than 90% for a spiking of 50 μg), while from dry XAD-2 resin recovery is less than 10%. By humidifying the XAD-2 cartridge the recovery has been improved up to 80%. Sampling lab simulations have shown a recovery of slightly less than 60%, when the compound is added (50 μg) to the first XAD-2 cartridge; the hexamethylphosphotriamide hasn't been found nor onto the second XAD-2 cartridge nor into the condensate.

The field tests, with the same spiking modalities, have shown a recovery rate of 27% with a standard deviation of 47%, thus confirming the results of previous Authors and the inadequacy of US-EPA 0010 train. More promising results have been given by the KOH solution method. Laboratory tests have shown typical recovery of 104% (with 18% RSD) for a 40 mL solution spiked with 50 μg of hexamethylphosphotriamide.

Sampling train tested with lab simulated emissions has also given satisfactory results: $98\pm 9\%$ recovery has been achieved for 100 μg spiked into the first washing bottle. On-site sampling have given less satisfactory results: 50 μg spike has been recovered with a rate of $41\pm 1\%$. Hexamethylphosphotriamide has been found only into the first washing bottle, probably because of degradation during the sampling. Despite the fact that recovery rate has been shown less than US-EPA acceptability criteria, the method seems with no alternatives. Spiking is necessary, to keep into account degradation phenomena during sampling.

2-naphthylamine, 3,3'-dimethoxybenzidine, 3,3'-dichlorobenzidine, 3,3'-dimethylbenzidine, 4,4'-methylenebis(2-chloroaniline), 4-aminobiphenyl, Benzidine. These compounds show high reactivity and tend to decompose during sampling [Johnson 1999]. US-EPA 0010 sampling train has given not satisfactory results,

and some compounds are analyzed by GC with difficulty. To extract the compounds from XAD-2 cartridges, a heated Soxhlet procedure has been shown necessary, with extraction rates between 70 and 130% (with RSD of 10-18%), with the exception of benzidine, for which recovery rates of 17-37% have been obtained. Also the extraction from condensate has been shown difficult: some amines, in fact, tend to form salts with sulfate ions and it is necessary to perform an extraction at two pH values (2 and 13), in order to get quantitative recovery rates. Field tests have been performed, with US-EPA 0010 train, by spiking the first XAD-2 cartridge with 10 µg of each compound. Analysis results have shown recovery less than 40 %.

Better results have been obtained with the method of sampling onto sulfuric acid impregnated filters [OSHA 1989 a,b; OSHA 1992a]. For the 3,3'- dimethoxybenzidine, not covered by the OSHA methods quoted above, preliminary tests have been made, in order to check the suitability of the procedure used for all other compounds. Laboratory recovery rates, obtained by spiking a series of filters with 100 ng of each compound, have been shown better than 80% (with 20% RSD). Simulated emissions sampling have given the following results:

- only humidified hot air: recovery rates better than 80% (4—24% RSD), except for 4-aminobiphenyl and 3,3'- dimethoxybenzidine (60% rate);
- with the addition of SO₂: significant reduction of method performances;
- with SO₂ and NO_x addition: satisfactory results for 3,3'-dimethylbenzidine, 4,4'-methylenebis(2-chloroaniline) and benzidine, while for 3,3'-dichlorobenzidine, 3,3'- dimethoxybenzidine and 4-aminobiphenyl a recovery rate less than 70% has been obtained. For 2-naphthylamine a 100% average recovery rate has been obtained, but with too high RSD to be accepted according to US-EPA criterion.

No compounds have been detected onto the second filter, confirming the hypothesis of degradation or reactions into the sampling train.

For on-site tests, a series of impregnated filters have been spiked (at the lab) with 200 ng of each compound; some filters have been stored on-site, in order to verify their stability. The analysis of this last set of filters has shown quantitative recovery (80% with 20%RSD and 75% for benzidine only). Sampled filters analysis has shown very good results for benzidine, 3,3'-dichlorobenzidine and 4,4'-methylenebis(2-chloroaniline), while for all other compounds recovery rates less than 70% but with very limited RSD (less than 4%) have been obtained. Aromatic compounds have been always found onto the first filter only.

Diethyl sulfate and Dimethyl sulfate. Dimethylsulfate is a very reactive compound, water soluble and decomposable. According to Johnson [Johnson 1999] there are no suitable methods for its determination in combustion processes emissions. Diethylsulfate is less humidity sensitive, but reactive. In the present work a method based on Tenax sampling [Krost 1982] has been used. Some preliminary lab tests allowed the determination of breakthrough volume for the selected Tenax cartridges in about 10 L; therefore a maximum sampling volume of 5 L has been fixed. A second problem to be faced with was the exhaust humidity condensation inside the cartridge: a series of cartridges have then been spiked with 10 ng of each compound and with 200 µL of water acidified with sulfuric acid (to simulate condensate). Increasing nitrogen volumes (from 0.2 to 5 L) have been sampled, at a flow rate of 150 mL/min, keeping the cartridges at room temperature and at 50 °C. The test with the cartridges maintained at 50 °C showed a 60% (or greater) loss of the compounds; at room temperature, 3 L nitrogen were enough to dry the cartridge: in these conditions a recovery greater than 90% has been obtained.

Sampling simulated emissions, with the laboratory test rig, always showed recovery rates fully acceptable, i.e. for dimethylsulfate 76—93% and for diethylsulfate 82—94%, with—in both cases- RSD less than 15%.

For the field tests the cartridges have been spiked with 200 ng of dimethylsulfate and 170 ng of diethylsulfate. As usual, some spiked cartridges have been brought on site, for storage procedure testing: recovery rates from these cartridges have been as follows: 101% (RSD=1%) for diethylsulfate and 87% (RSD=2%) for dimethylsulfate. Analysis of the sampling cartridges have shown recovery of 99 and 83% for dimethylsulfate and diethylsulfate respectively. Some sampling with non spiked cartridges have been performed, in order to check the presence of the target compounds in the flue gases, but none showed concentration above detection threshold.

Hydrazine and N,N'-dimethylhydrazine. Both compounds are strongly reactive and water soluble, and no method suitable for flue gases exists [Johnson 1999, Radian Corporation 1991]. Three sampling methods have been analyzed, i.e. US-EPA 0010, US-EPA 0031 (VOST) and use of HCl 0.1N solution. From the preliminary lab tests, the first two methods showed a great deal of problems: recovery rate from 0010 train less than 10%, no

suitable thermal desorption method for 0031 train sampling supports. The method based on HCl solution showed recovery rates from 100 µg spiked solutions better than 90%.

Field tests have been performed, with a sampling train comprising three series washing bottles, containing 50 mL of HCl 0.1 N solution; the solution of the first washing bottle has been spiked with 100 µg of the target compounds. Both compounds have been quantitatively recovered from the first washing bottle, with average rates of 95±5 % for hydrazine and 106±9 % for N,N'-dimethylhydrazine. In the samplings with non spiked solutions both compounds have never been found above detection limit (1 µg/15 mL).

Sulfallate, 1,2-dibromoethane, 2-nitropropane, 3-propanolyde, 1,3-propane sultone, epychloridrin, dimethylcarbamoilchloride, styrene oxide. For these compounds, the US-EPA 00101 method has been tested. Preliminary lab tests have then been performed, in order to verify the recovery rates of extraction phase. To evaluate the eventual losses during the evaporation of the solvent used for extraction, 50 µg of each compound have been added to 200 mL of dichloromethane and solutions have been concentrated to 1 mL volume in rotating evaporator. Average recovery rates have been as follows: 80% (RSD=9%) for 1,2-dibromoethane, 101% (RSD=19%) for 2-nitropropane, 77% (RSD=3%) for 1,3-propane sultone, 88% (RSD=3%) for sulfallate, 90% (RSD=4%) for 3-propanolyde. Epychloridrin and styrene oxide showed, on the other side, recovery rates less than 10%. Therefore, for the other compounds, recovery tests from filters have been made, with very similar results to those of extraction.

Recovery tests from XAD-2 cartridges, again spiked with 50 µg of each compound, showed the following rates: 64% (RSD=21%) for 1,2-dibromoethane, 74% (RSD=11%) for 2-nitropropane, 71% (RSD=4%) for 1,3-propane sultone, 60% (RSD=4%) for sulfallate, 73% (RSD=2%) for 3-propanolyde. All these values are lower than those obtained for filters, showing a more difficult recovery from XAD-2 resin, maybe due to retention problems.

Sampling of simulated emissions have been performed by spiking filters with 50 µg of each compound; 1 m³ of exhaust gases, with 10% water, 600 mg/m³ SO₂ and 200 mg/m³ NO_x, has been sampled. The compounds have been found only in the first XAD-2 cartridge, while they were absent in filters, condensate and second XAD-2 cartridges. According to US-EPA acceptability criterion, the method has been proven suitable for 2-nitropropane, 1,3-propane sultone and 3-propanolyde, while smaller rates have been reported for sulfallate, 1,2-dibromoethane. Recovery appeared more difficult than those from filters and XAD-2 resins, so indicating some losses or degradation inside the sampling train.

Field tests have been performed, by spiking only the first XAD-2 cartridge. Some XAD-2 cartridges have been brought on-site, in order to test storage procedure; during this phase, some losses have been detected, up to 40%. A correction factor has therefore been applied to the recovery from the supports used in the samplings; for 2-nitropropane, 1,2-dibromoethane, 1,3-propane sultone and sulfallate the results can be deemed acceptable. Storage and extraction procedures shall be improved, and some modification to the sampling train shall be made, in order to improve its chemical inertia.

Ethylentiourea. Ethylentiourea is a semi-volatile compound, water soluble (1-5 mg/L) and sensitive to the light exposure. The use of US-EPA 0010 method is deemed difficult, because of its reactivity; the recovery from XAD-2 resins appeared difficult and no satisfactory response has been obtained by gaschromatography. For all these reasons, a method based on sampling with glass fiber filters and washing bottles filled with deionized water, and analysis by HPLC/UV has been chosen. Two different alternatives for sampling have been tested: A) sampling train with two glass fiber filters in series and one washing bottle with 10 mL of deionized water (sampling flow rate 3 L/min); B) sampling train with two washing bottles with 30 mL of deionized water, refrigerated at 5 °C (sampling flow rate 15 L/min).

In the lab some filters have been spiked with 50 µg of ethylentiourea and then extracted by ultrasonic bath for 10 min with 5 mL of deionized water, with an average recovery rate of 95% (RSD=3%). At the same time some samples of condensate coming from oil fired combustion plants have been analyzed, in order to evaluate the possible analytical interferences. Once that no interferences have been found, condensate samples have been spiked with ethylentiourea and analyzed again, with good results (recovery rate greater than 90%).

The type A sampling train has been field tested: 200 µg of ethylentiourea have been spiked onto the first filter, and 60 L exhaust gases have been sampled, at a flow rate of 2 L/min (note that the filters have been maintained at 120 °C, the same temperature of flue gases). The analyses have shown that the ethylentiourea was no more present in the first and in the second filters, being recovered from the condensate; average recovery rate was only 40% and therefore this method was judged unsuitable for combustion emissions.

The type B) train has been also field tested, filling the two washing bottles with 50 mL of deionized water and setting a flow rate of 15 L/min (for a total volume of 1 m³). In the first washing bottle 500 µg of ethylthiourea have been deposited and the two bottles have been kept refrigerated (5±10 °C) for the whole sampling. Ethylthiourea has been found in both washing bottles, but a definite trend was not detected; average recovery rate was 60% (RSD=20%). Another series of sampling has then been performed, with a reduced flow rate (from 15 to 2 L/min) and with a larger number of washing bottles (from 2 to 4), the first again spiked with 500 µg of the compound. With this arrangement, the recovery rate has been increased up to 98% (RSD=5%).

Sampling with non spiked train didn't show the presence of ethylthiourea above the detection limit of the method (i.e. 0.05 µg/mL).

Acrylonitrile. Three methods have been tested, i.e.: bubbling into water solutions, solid adsorbents (US-EPA 0031 Method), bubbling into methanol solution followed by a solid adsorbent. Sampling trains have been directly tested on-site, while in the lab only analytical techniques have been developed.

US-EPA 0031 sampling train didn't give satisfactory results, showing an almost complete loss of acrylonitrile.

Sampling with aqueous solution have been made with the same train used for ethylthiourea, i.e. four washing bottles, the first of which with 10 mL of deionized water and the other with 30 mL of water each. In the first washing bottle 100 µg of acrylonitrile has been deposited, as methanol solution. Sampled volume has been 50 L at 2 L/min flow rate. During sampling all washing bottles have been kept refrigerated at 5 °C. Acrylonitrile has been extracted from the solutions according to the US-EPA method 8031 and analyzed by GC/NPD. Despite the extreme simplicity of this sampling train, its use cannot be recommended, because substantial losses of the target compound have been detected.

More promising results have been obtained with the sampling train composed of methanol filled washing bottles followed by an activated charcoal trap. The washing bottle have been spiked with 30 µg of acrylonitrile. Analyses performed via GC/NPD have shown a recovery rate better than 75%; moreover, 90% of the recovered compound comes from the methanol solution, while the remaining 10% comes from the activated charcoal trap. In the samplings performed using non spiked washing bottle no acrylonitrile has been found, with a detection limit of 0.05 µg/mL.

Styrene oxide and ethylene oxide. For both compounds the suitability of NIOSH method N.1614 has been verified. This method has been developed for the determination in ambient air of ethylene oxide, and in the present work it has been deemed applicable also for styrene oxide, due to the chemical affinity of the two compounds. The method requires the sampling with activated charcoal traps, coated with HBr. The compounds are then desorbed with DMF, derivatized with N-heptafluorobutyrylimidazol and analyzed by GC/ECD. The method has been tested directly on-site, using traps spiked with both compounds. The results have been negative, because of the high level of analytical interferences and of the relevant losses from sampling supports. US-EPA 0040 method (sampling with Tedlar bags) has been verified for ethylene oxide only. The main problem encountered with this method is the instability of the compound, which tends to disappear in a few hours after being sampled into the Tedlar bags.

For styrene oxide, direct sampling onto Tenax cartridges has been also tested. The compound is then eluted from Tenax with ethyl acetate and analyzed by GC/FID with a Supelco SPB-5 capillary column. A series of flue gases sampling has been performed with two Tenax cartridges in parallel, one with 250 µg of styrene oxide spike and one without. The comparison of chromatographic profiles showed the complete loss of the compound and the formation of degradation products: GC/MS analysis proved this product to be phenyl acetaldehyde. Both styrene and ethylene oxides require therefore the development of a suitable method for combustion processes emissions.

Volatile compounds. In this class many compounds have been included, i.e.: epichlorohydrin, propylene oxide, 1,2-dichloroethane, 1,3-dichloro-2-propanol, acrylonitrile, benzene, 1,2-dibromoethane, 2-nitropropane, hydrazine, ethylenimine, 3-propanolyde, chloromethyl(methyl)ether, bis-chloromethylether. Many of them are reactive and/or water soluble. Two methods have been tested, i.e. the US-EPA 0031 (VOST) and direct sampling with activated charcoal (eventually with dilution probe). US-EPA 0031 method didn't perform satisfactorily.

Preliminary lab tests allowed to verify the good recovery rates from activated charcoal cartridges for propylene oxide (91±4%), 1,3-dichloro-2-propanol (83±9%), epichlorohydrin (84±13%). On-site tests have also been performed, by spiking charcoal traps with 15-25 µg of the compounds and sampling 50 L of flue gases, at a flow

rate of 1 L/min. Recovery rate (see Table 4) did not meet US-EPA acceptability criterion, but nevertheless appeared encouraging enough to continue the development work.

Very volatile compounds. In this class have been included the following compounds: vinyl chloride, 1,3-butadiene, propylene oxide; also benzene and 1,2-dichloroethane have been included, because they are volatile enough to satisfy the US-EPA 0040 method criteria. The tests have been made by flue gases sampling into several 10 L Tedlar bags, with and without dilution. The bags have been spiked with 300 ng of the target compounds and transferred to the lab. The analysis has been performed by GC/MS, by sampling 50 mL of gas onto a Supelco Carbotrap200 cartridge, which is the thermally desorbed into the gaschromatographic column.

Recovery rates (see Table 4) are acceptable for 1,3-butadiene, benzene and 1,2-dichloroethane; there are no differences between Tedlar bags with or without humidity. Propylene oxide GC/MS analysis resulted very difficult and some controls are now being performed, aimed to optimize the analytical method.

Polychloronaphtalenes (PCN). The greatest analytical difficulty is the determination of all possible PCN congeners. In this work, the Heinemann procedure (see previous chapter) has been adopted. As a sampling method the US-EPA 0010 has been chosen. Extraction procedures have been verified in the lab: after a spiking with 100 µg of PCN (using a commercial Halowax mixture), it has been shown that the average recovery rate is for filters 103% (RSD=4%) and for condensate 92% (RSD=6%); from XAD-2 cartridges the recovery appeared more difficult, with an average of 72% (RSD 24%).

The method has then been tested on-site: two series of tests have been made, the first with the spiking of 106 µg of Halowax onto the filter, and the second with the same spiking onto the first XAD-2 cartridge. In the first series of tests, PCN have been volatilized from the spiked filter and have been found in the washing solution and in the first two XAD-2 cartridges. Average recovery rate has been 61% (RSD=12%), so showing some losses inside the sampling train, maybe due to some active site in the glassware of the condenser. In the second series of tests, 15-20% of deposited PCN have been found in the second XAD-2 cartridge. Average recovery has been 75% (RSD=20%). No PCN in the flue gases have been found when using non spiked sampling supports.

Polychloroterphenyls (PCT). For PCT the US-EPA 0010 method has been used. Extraction procedures have been verified in the lab, by spiking 2 µg of total PCT (from a commercial mixture, Aroclor 5460) onto the solid supports. Recovery rates have been as follows: 85±9% for filters, 101±10% for XAD-2 cartridges, 91±16% for the condensate. As for PCN, the method has then been tested on-site with two series of tests: the first with the spiking of 500 ng of Aroclor5460 onto the filter, and the second with the same spiking onto the first XAD-2 cartridge.

In the first series of tests, PCN have been recovered for more than 60% from filters and for 20÷30% in the condenser washing, and no PCT have been found in the XAD-2 cartridges; global average recovery has been 95±10%. Also in the second series of tests, PCT have been recovered quantitatively (125±8%) and none compound have been found in other parts of the sampling train. In the samplings with non spiked supports PCT haven't been found. The method has passed the US-EPA acceptability criterion, but still remains the problem of the absence of PCT formulation to be used as a reference in the quantitative analysis. A possible approach to solve this problem is as follows:

- samples are analyzed by GC/ECD and the PCT presence is checked in the relevant chromatogram area;
- if no peaks are detected, the analysis is terminated and the detection limit (D.L.) can be calculated with the aid of a standard PCT mixture;
- if in the GC/ECD analysis some peak appears, the analysis should be repeated by means of GC/MS, in order to confirm the PCT presence;
- if no PCT are qualitatively detected by GC/MS their presence can be excluded and it is possible to use the D.L. calculated from GC/ECD;
- if PCT presence is confirmed, a quantitative analysis can be made by GC/ECD, using the total area method.

4 Conclusions

Italian Law on emission limitation and control requires 54 organic compounds to be determined in the flue gases of industrial combustion plants.

Experimental tests performed allowed to select and verify –at least in a preliminary way- a series of procedures suitable for the sampling in combustion flue gases of about 30 organic pollutants (see Table 5).

At the present work stage no suitable methods have been developed for the following compounds: dimethyl carbamoyl chloride; ethylenediamine; acrylonitrile; chloromethyl methyl ether; ethylene oxide; bis(chloromethyl) ether; 3-propanolide (beta-propiolactone); styrene oxide.

The majority of these compounds are very volatile and reactive and in some cases even not stable.

Future development of the work will imply to go deeper into the technical literature, in order to find out better suggestion about sampling methods and materials, and to perform further lab and field tests.

References

- Bertolaccini M.A., D'Innocenzo F., Marconi A. 1991. Metodi di analisi degli inquinanti nelle emissioni da impianti fissi. Rapporto ISTISAN 91/31
- Johnson L.D 1999. Methods 98 – Status of Stationary Source Methods for Air Toxics. Available for downloading from: <http://www.epa.gov>
- Heidmann W.A. 1988. Isomer specific determination of polychlorinated technical mixtures such as polychloronaphthales by GC/MS. *Chromatographia*, 25: 8 –14.
- Krost K.J., Pellizzari E.D., Walburn S.G., Hubbard S.A. 1982. Collection and analysis of hazardous organic emissions
- *Anal. Chem.* 54: 810-817
- NIOSH 1994a. Method 3503: hydrazine. *Manual of Analytical Methods*, 4rd ed
- NIOSH 1994b. Method 3515: 1,1-dimethylhydrazine. *Manual of Analytical Methods*, 4rd ed
- NIOSH 1994c. Method 5011: Ethylene Thiourea. *Manual of Analytical Methods*, 4rd ed
- OSHA 1989a. Method 65: benzidine; 3,3'-dichlorobenzidine; 2,4-toluenediamine; 2,6-toluenediamine. *Analytical Method Manual*.
- OSHA 1989b. Method 71: o-Dianisidine; 4,4'-methylenebis(2-chloroaniline); o-tolidine. *Analytical Method Manual*.
- OSHA 1992a. Method 93: 4-aminobiphenyl; 1-naphthylamine; 2-naphthylamine. *Analytical Method Manual*.
- OSHA 1992b. Method 95: Ethylene Thiourea. *Analytical Method Manual*
- Rounbehler D.P., Reisch J.R., Coombs J.R., Fine D.H. 1980. Nitrosamine Air Sampling Sorbents Compared for Quantitative Collection and Artifact Formation. *Anal. Chem.*, 52: 273-276
- UNI 1996. Metodo 10493. Misure alle emissioni. Determinazione di sostanze organiche volatili per adsorbimento su carboni attivi ed analisi gascromatografica.
- UNICHIM 1989. Metodo 825. Misure alle emissioni. Campionamento e determinazione di microinquinanti organici.
- US-EPA 1986a. Modified Method 5 Sampling Train. Method 0010, rev. 0. *Test Methods for Evaluating Solid Waste: Physical/Chemical Methods*. SW – 846, 1986
- US-EPA 1986b. Extraction of semivolatile analytes using method 0010 (Modified Method 5 Sampling Train). Method 3542, rev. 0. *Test Methods for Evaluating Solid Waste: Physical/Chemical Methods*. SW – 846
- US-EPA 1987. Method 301. Protocol for the Field Evaluation of Emissions Concentrations from Stationary Sources. Code of Federal Regulations, Title 40, Part 63, Washington DC. Office of Federal Register, 1987
- US-EPA 1994,. Method 8031. Acrylonitrile by Gas Chromatography. *Test Methods for Evaluating Solid Waste: Physical/Chemical Methods*. SW – 846.
- US-EPA 1996a. Sampling Method for Volatile Organic Compounds (SMVOC). Method 0031, rev. 0. *Test Methods for Evaluating Solid Waste: Physical/Chemical Methods*. SW – 846
- US-EPA 1996b. Sampling of principal organic hazardous constituents from combustion sources using Tedlar bags. Method 0040, rev. 0. *Test Methods for Evaluating Solid Waste: Physical/Chemical Methods*. SW – 846
- US-EPA 1998. Conditional Test Method for Acrylonitrile (CTM-008). Available for downloading from: <http://www.epa.gov/ttnemc01/ctm.html>
- Wagoner D.E., Merrill R.G., McGaughery J.F., Bursley J.T. 1991. Evaluation of CAA Compounds: Approaches for Stationary Source Method Development. US-EPA Report 600/SR-96/091

The Author

Antonio Negri
Business Unit ENVIRONMENT
CESI Spa
Via Reggio Emilia, 39
20090 Segrate (Milan)
Italy
Tel.: +39.02.2125.8119
FAX: +39.02.2125.8691
e-mail: negri@cesi.it

Antonio Negri received a degree in Nuclear Engineering from Politecnico of Milan in 1979. He is working in the energy and environment field since 20 years, with special attention to atmospheric pollution. He manages the Atmospheric Pollution Line, within the Environment Business Unit of CESI, which provides R&D activities and services in the fields of emission monitoring and inventory, atmospheric modeling, air quality monitoring, indoor pollution, greenhouse gases monitoring and climatic changes study.

Table 1 – List of examined compounds

| Compound | CAS | Tab. ¹ | Class ¹ | Emission limit value ¹ [mg/m ³] | Italian official methods |
|---|-----------|-------------------|--------------------|--|--------------------------|
| 2-naphthylamine | 91-59-8 | A1 | 1 | 0.1 | None |
| N – nitrosodimethylamine | 62-75-9 | A1 | 1 | 0.1 | None |
| 3,3'- dimethoxybenzidine | 119-90-4 | A1 | 2 | 1 | None |
| 3,3'-dichlorobenzidine | 91-94-1 | A1 | 2 | 1 | None |
| 3,3'-dimethylbenzidine | 119-93-7 | A1 | 2 | 1 | None |
| 4,4'-methylenebis(2-chloroaniline) | 101-14-4 | A1 | 2 | 1 | None |
| 4-aminobiphenyl | 92-67-1 | A1 | 2 | 1 | None |
| Benzidine | 92-87-5 | A1 | 2 | 1 | None |
| Diethyl sulfate | 64-67-5 | A1 | 2 | 1 | None |
| dimethyl carbamoyl chloride | 79-44-7 | A1 | 2 | 1 | None |
| Dimethyl sulfate | 77-78-1 | A1 | 2 | 1 | None |
| Hexamethylphosphoramide | 680-31-9 | A1 | 2 | 1 | None |
| sulfallate | 95-06-7 | A1 | 2 | 1 | None |
| 1,2-dibromoethane | 106-93-4 | A1 | 3 | 5 | None |
| 1,2-dichloroethane | 107-06-2 | A1 | 3 | 5 | UNI 10493 |
| 1,2-epoxypropane (propylene oxide) | 75-56-9 | A1 | 3 | 5 | None |
| 1,3-butadiene | 106-99-0 | A1 | 3 | 5 | None |
| 1,3-dichloro-2-propanol | 96-23-1 | A1 | 3 | 5 | None |
| 1,3-propane sultone | 1120-71-4 | A1 | 3 | 5 | None |
| 1-chloro-2,3-epoxypropane (epichlorohydrin) | 106-89-8 | A1 | 3 | 5 | None |
| 2-nitropropane | 79-46-9 | A1 | 3 | 5 | None |
| 3-propanolide (beta-propiolactone) | 57-57-8 | A1 | 3 | 5 | None |
| acrylonitrile | 107-31-1 | A1 | 3 | 5 | None |
| benzene | 71-43-2 | A1 | 3 | 5 | UNI 10493 |
| bis(chloromethyl)ether | 542-88-1 | A1 | 3 | 5 | None |
| chloromethyl methyl ether | 107-30-2 | A1 | 3 | 5 | None |
| Ethylenethiourea | 96-45-7 | A1 | 3 | 5 | None |
| Hydrazine | 302-01-2 | A1 | 3 | 5 | None |
| N,N'-dimethylhydrazine | 57-14-7 | A1 | 3 | 5 | None |
| ethylene oxide | 75-21-8 | A1 | 3 | 5 | None |
| stirene ossido | 96-09-3 | A1 | 3 | 5 | None |
| vinyl chloride | 75-01-4 | A1 | 3 | 5 | None |
| PCN | | A2 | 1 | 0.5 | DM 25/8/2000 n.158 |
| PCT | | A2 | 1 | 0.5 | DM 25/8/2000 n.158 |

(1) Italian Law: decree of Environment Ministry July 12, 1990 N.51

Table 2 - Grouping of the 36 investigated compounds and preliminary definition of the potentially suitable methods (reactive and water soluble compounds are bolded)

| Groups | Compounds | Examined/tested methods | |
|---------------------------------------|---|--|--|
| | | Sampling | Analysis |
| Polyaromatics | PCN | US-EPA SW 846-0010 | GC/MS |
| | PCT | | GC/ECD and GC/MS |
| Semi volatile organics | Sulfallate, 1,2-dibromoethane, 2-nitropropane, 3- propanolyde, 1,3-propane sultone, hexamethylphosphoramide epichlorhydrin, dimethyl carbamoil chloride , styrene oxide | US-EPA SW 846-0010 | GC/MS |
| | Hexamethylphosphoramide | Washing bottles with diluted NaOH | GC/FID |
| | Ethylenethiourea | US-EPA SW 846-0010 | GC/MS |
| | | Condensate collection | HPLC/UV |
| | 2-naphthylamine, 3,3'- dimethoxybenzidine, 3,3'- dichlorobenzidine, 3,3'-dimethylbenzidine, 4,4'-methylenebis(2-chloroaniline), 4-aminobiphenyl, Benzidine | US-EPA SW 846-0010 | GC/MS |
| Sulfur compounds | Diethyl sulfate, Dimethyl sulfate | US-EPA SW 846-0010 | GC/MS |
| | | Tenax cartridges | Thermal desorption coupled with GC/FPD |
| Volatiles and very volatiles organics | 1,3-butadiene, vinyl chloride, 1,2-epoxypropane , benzene, 1,2-dichloroethane | US-EPA 0040 (sampling with Tedlar bags) | GC/MS |
| | propylene oxide, ethylenimine, chloromethyl(methyl)ether, N-N'-dimethylhydrazine, acrylonitrile , benzene, 1-2dichloroethane, bis-chloromethylether , hydrazine, epichlorhydrin, 2-nitropropane , 1-2dibromoethane, beta-propiolattone, dimethylcarbamoilchloride | US-EPA 0031 (VOST) | Thermal desorption and GC/MS |
| | propylene oxide, epichlorhydrin , 1-3-dichloro-2-propanol | Dilution probe and active charcoal vials | GC/FID |
| | Acrylonitrile | Bubbling into methanol and charcoal trap | GC/NPD |
| | | Bubbling into deionized water | GC/NPD |
| Oxides | Ethylene oxide and styrene oxide | Active charcoal vial HBr impregnated | |
| | | US-EPA 0040 (sampling with Tedlar bags) | GC/MS |
| Hydrazines | N,N'-dimethylhydrazine Hydrazine | US-EPA SW 846-0010 | GC/MS |
| | | Washing bottles with HCl 0.1 N | Colorimetry |
| | | US-EPA 0031 (VOST) | Thermal desorption and GC/MS |
| Nitrosoamine | N – nitrosodimethylamine | Washing bottles with dilutedNaOH | GC/FID |
| | | Thermosorb /P | GC/FID |

Table 3 – Sampling simulations results. Average percent recovery rates (in parenthesis the Relative Standard Deviation)

| | | | A | B | C | D | |
|------------------------------------|--|---|--------------------------------------|---------|---------|----------|-----|
| | | | Humidity (%) | 0 | 10 | 10 | 10 |
| | | | SO ₂ (mg/m ³) | 0 | 0 | 600 | 600 |
| | | | NOx (mg/m ³) | 0 | 0 | 0 | 200 |
| Compound | Quantity | Sampling train | | | | | |
| N-N'-dimethylnitrosoamine | 10-100 µg in the first washing bottle | 4 washing bottles in series with NaOH 1 N | - | - | - | 79 (6) | |
| | 10-100 µg injected in the heated sampling line | | - | - | - | 85 (5) | |
| Hexamethylphosphoramide | 100 µg in the first washing bottle | 4 washing bottles in series with NaOH 1 N | - | - | - | 98 (9) | |
| | 50 µg onto the first XAD-2 cartridge | US-EPA 0010 Method | - | - | - | 57 (3) | |
| 2-naphtylamine | 100 ng | Sulfuric acid impregnated filters | - | 85 (24) | 80 (27) | 100 (64) | |
| 4-aminobiphenyl | 100 ng | | - | 19 (9) | 17 (9) | 41 (64) | |
| Benzidine | 100 ng | | - | 102 (4) | 67 (6) | 82 (81) | |
| 3,3'-dichlorobenzidine | 100 ng | | - | 93 (13) | 58 (7) | 60 (14) | |
| 4,4'-methylenebis(2-chloroaniline) | 100 ng | | - | 104 (5) | 69 (9) | 80 (15) | |
| 3,3'-dimethoxybenzidine | 100 ng | | - | 56 (13) | 46 (4) | 44 (13) | |
| Dimethylsulfate | | Tenax | 110 (13) | 84 (1) | 76 (6) | 93 (2) | |
| Diethylsulfate | | | 83 (12) | 87 (2) | 82 (8) | 94 (1) | |
| 2-nitropropane | 50 µg | US-EPA 0010 | - | - | - | 56 (24) | |
| 3-propanolide | 50 µg | US-EPA 0010 | - | - | - | 78 (5) | |
| 1,2-dibromoethane | 50 µg | US-EPA 0010 | - | - | - | 43 (16) | |
| 1,3 propane sultone | 50 µg | US-EPA 0010 | - | - | - | 68 (4) | |
| Sulfallate | 50 µg | US-EPA 0010 | - | - | - | 47 (3) | |

Table 4 – Field tests results. Average percent recovery rates (in parenthesis the Relative Standard Deviation)

| Compound | Quantity | Sampling train | Recovery % (RSD%) |
|------------------------------------|--|--|-------------------|
| N,N'-dimethylnitrosoamine | 10µg in the first washing bottle | 4 washing bottles in series with NaOH 1 N | 70 (2) |
| Hexamethylphosphorotriamide | 100 µg in the first washing bottle | 4 washing bottles in series with NaOH 1 N | 41 (1) |
| | 50 µg onto the first XAD-2 cartridge | US-EPA 0010 Method | 14 (47) |
| 2-naphthylamine | 200 ng on the first filter | 2 series sulfuric acid impregnated filters | 85 (15) |
| 4-aminobiphenyl | 200 ng on the first filter | | 90 (20) |
| Benzidine | 200 ng on the first filter | | 75 (26) |
| 3,3'-dichlorobenzidine | 200 ng on the first filter | | 95 (28) |
| 3,3'-dimethylbenzidine | 200 ng on the first filter | | 98 (27) |
| 4,4'-methylenebis(2-chloroaniline) | 200 ng on the first filter | | 85 (23) |
| 3,3'-dimethoxybenzidine | 200 ng on the first filter | | 85 (23) |
| Dimethylsulfate | 200 ng | Tenax | 99 (2) |
| Diethylsulfate | 170 ng | | 83 (12) |
| 2-nitropropane | 50 µg on the 1 st XAD-2 cartridge | US-EPA 0010 | 77 (10) |
| 3-propanolyde | 50 µg on the 1 st XAD-2 cartridge | US-EPA 0010 | < 1 |
| 1,2-dibromoethane | 50 µg on the 1 st XAD-2 cartridge | US-EPA 0010 | 67 (30) |
| 1,3 propane sultone | 50 µg on the 1 st XAD-2 cartridge | US-EPA 0010 | 90 (47) |
| Sulfallate | 50 µg on the 1 st XAD-2 cartridge | US-EPA 0010 | 62 (10) |
| Ethylthiourea | 500 µg in the first bottle | 4 washing bottles in series with deionized water | 98 (5) |
| Acrylonitrile | 100 µg | Washing bottle with methanol and activated charcoal trap | 78, 79 |
| Propylene oxide | 12.5 µg | Activated charcoal trap (dilution probe) | 62 (14) |
| 1,3-dichloro-2-propanol | 25 µg | Activated charcoal trap (dilution probe) | 65 (26) |
| 1-chloro-2,3-epoxypropane | 12.5 µg | Activated charcoal trap (dilution probe) | 54 (23) |
| 1,3-butadiene | 24 µg | Tedlar bag | 95 (10) |
| Vinyl chloride | 50 µg | Tedlar bag | 90 (15) |
| Benzene | 44 µg | Tedlar bag | 94 (7) |
| 1,2-dichloroethane | 63 µg | Tedlar bag | 92 (12) |
| PCN | 106 µg on the filter | US-EPA 0010 | 61 (12) |
| | 106 µg on the first XAD-2 cartridge | US-EPA 0010 | 75 (20) |
| PCT | 500 ng on the filter | US-EPA 0010 | 95 (10) |
| | 500 ng on the first XAD-2 cartridge | US-EPA 0010 | 125 (8) |

Table 5 – Synopsis of the methods which showed the best performances is presented.

| Compound | CAS | Emission Limit Value ELV [mg/m ³] | Sampling method | Analysis method |
|---|--|---|--|--|
| N - nitrosodimethylamine Hexamethylphosphoramide | 62-75-9 680-31-9 | 0,1 1 | Impinger with NaOH 1 N solution | Extraction with dichloromethane and GC/FID analysis |
| 2-naphthylamine 3,3'- dimethoxybenzidine 3,3'-dichlorobenzidine 3,3'-dimethylbenzidine 4,4'-methylenebis(2-chloroaniline) 4-aminobiphenyl Benzidine | 91-59-8 119-90-4 91-94-1 119-93-7 101-14-4 92-67-1 92-87-5 | 0,1 1 1 1 1 1 1 | Sulfuric acid impregnated double filters | Extraction with water, basification, 2 nd extraction with toluene, derivatization with heptafluorobutyric anhydride and GC/ECD analysis |
| Diethyl sulfate Dimethyl sulfate | 64-67-5 77-78-1 | 1 1 | Adsorption on Tenax cartridge | Thermal Desorption coupled with GC/FPD |
| Benzene 1,3-butadiene vinyl chloride | 71-43-2 106-99-0 75-01-4 | 5 | Flue gases collection in Tedlar bags | GC/MS |
| 1-chloro-2,3-epoxypropane (epichlorohydrin) 1,2-epoxypropane (propylene oxide) 1,2-dichloroethane 1,3-dichloro-2-propanol | 106-89-8 75-56-9 107-06-2 96-23-1 | 5 | Adsorption on activated charcoal | GC/FID GC/FID GC/MS GC/FID |
| N,N'-dimethylhydrazine Hydrazine | 57-14-7 302-01-2 | 5 | Bubbling in a HCl 0.1 N solution | Separated colorimetric determination |
| Ethylthiourea | 96-45-7 | 5 | Condensate collection | Direct analysis by HPLC/UV at 254 nm |
| Sulfallate (*) 1,2-dibromoethane 2-nitropropane (*) 1,3-propane sultone (*) | 95-06-7 106-93-4 79-46-9 1120-71-4 | 1 5 5 5 | According to US-EPA SW-846 Method 0010 | Extraction according to US-EPA SW-846 Method 3542; analysis by GC/MS |
| Acrylonitrile | 107-31-1 | 5 | Washing bottle with methanol and activated charcoal trap | GC/NPD |
| PCT PCN | | 0,5 | According to US-EPA Method 0010 | Extraction according to US-EPA SW-846 Method 3542; analysis by GC/ECD and confirmation by GC/MS. PCN analysis by GC/MS |

(*) possible losses during storage. Check with spiked blank is necessary