

Multi-Analyte Determination of Organic Contaminants in Incinerator Emissions and Ambient Air

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Abstract

A method has been developed that allows for the analysis of a wide range of organic contaminants commonly found in stack gas emissions and ambient air. These include the determination of PCDDs, PCDFs, PCBs, organochlorine and organophosphorus pesticides and PAHs from a single sample of either of these matrices. The combined sampling and analytical methods employed provide significant cost savings over existing methods, with little or no loss of method detection limits or analytical quality assurance. This method is of particular significance in impact assessment studies of stationary emission sources.

Introduction

Modern assessments of stationary emission sources and ambient air quality requires the measurement of a range of trace organic contaminants. This is often a complex task due to the diverse nature of the types of compounds that may be present. In recent years, particular attention has been paid to the formation and emission of polychlorinated aromatic compounds, including the polychlorinated dibenzo-p-dioxins (PCDDs), dibenzofurans (PCDFs) and polychlorinated biphenyls (PCBs) from such sources. In addition, other planar aromatic compounds, including the polycyclic aromatic hydrocarbons (PAHs) are also of particular environmental concern.

This laboratory has now developed a methodological approach for the determination of several multi-component groups of trace organic contaminants in stack emissions and ambient air. The method determines PCDDs, PCDFs, PCBs, PAHs, organochlorine pesticides (OCPs), organophosphorus pesticides (OPPs) as well as a range of other compounds from a single gaseous emission or ambient air sample.

Methods

Stationary source samples are collected using a procedure based on US EPA Method 5 for the isokinetic sampling of stack gas emissions. The sampling train consists in sequence of a heated filter compartment, XAD-2 resin trap followed by water then

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ethylene glycol impingers. Ambient air samples are collected using a General Metal Works PS-1 High Volume Air Sampler. The sample is pulled through a glass fibre filter and then a polyurethane foam (PUF) sandwich containing XAD-2 resin.

Prior to sampling, the XAD-2 resin of the MM5 train and the PUF sandwich of the ambient air sampler are spiked with a range of $^{13}\text{C}_{12}$ labelled surrogate PCDD, PCDF and PCB standards. In general, sampling is carried out until 1 m^3 of emission gas or 1000 m^3 of ambient air has been collected.

Prior to extraction, ^{37}Cl -TCDD and deuterated PAH surrogates are added to the sample. For emission samples, the resin and filter are Soxhlet extracted with toluene and the impinger liquids partitioned with dichloromethane. The two extracts are combined, evaporated and the crude organic extract made up to a known volume in solvent. This extract is then divided into appropriate fractions to provide for the determination of the following five multi-component groups. Following extraction, and immediately after the pesticide fraction is removed, the extract is again spiked with a further range of $^{13}\text{C}_{12}$ PCB standards. These PCB surrogates are added as a late spike so that any GC/ECD interferences in the analysis of the OCPs are avoided.

PCDDs and PCDFs: 50% of the crude extract is taken, partitioned with concentrated sulphuric acid and chromatographed from acid silica, silica, alumina and carbon. This series of chromatographic steps purifies the extract and allows for the separation of the PCB component. Analysis for PCDDs and PCDFs is by high resolution GCMS on a VG70 250S. Isomer specific determination is carried out for all 2378- chlorinated congeners. Non 2378- substituted PCDDs and PCDFs are determined as totals by isomer group.

PCBs: Chromatographic fractions from the PCDD and PCDF analysis are further purified through florisil prior to high resolution GCMS quantitation. The co-planar PCBs, mono-ortho and predominant di-ortho PCBs are determined isomer specifically.

PAHs: 20% of the crude extract is taken, further purified with dilute base, chromatographed through florisil and analysed by GCMS on a low resolution VG Trio 1000. All 16 US EPA priority pollutant PAHs are determined.

OPPs: 20% of the crude extract is taken, subject to gel permeation chromatography and analysed by capillary GC with detection by NPD and FPD. A total of 20 OPPs are routinely analysed for.

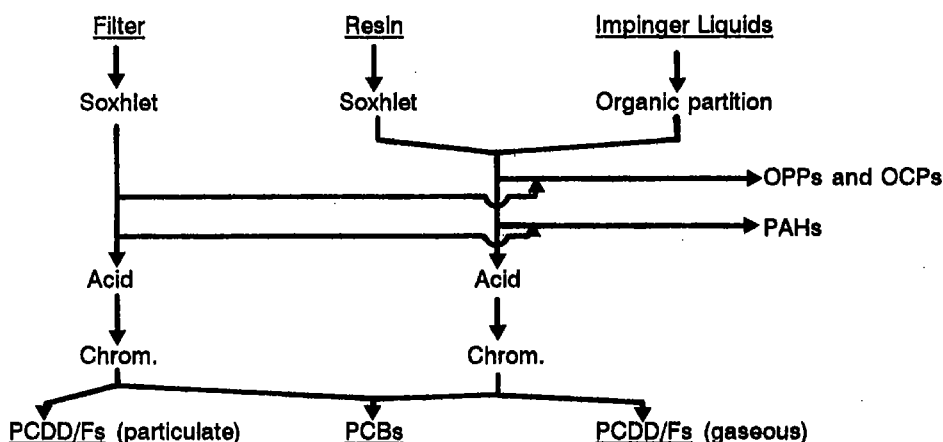
OCPs: Following analysis for OPPs, the remaining extract is further purified over florisil prior to analysis by GC ECD. 16 Persistent OCPs are determined.

Quantitation for PCDDs, PCDFs, PCBs and PAHs is by isotope dilution and for OPPs and OCPs by external standards.

Analysis of ambient air samples follows a similar procedure requiring initial Soxhlet extraction of the PUF/XAD-2 sandwich.

In certain instances, additional information may be obtained from the separate analysis of the filter (particulate component) and resin (gaseous component) of a stack emission sample. In such cases, and where a similar separation of the other analytes is not required, the methodological approach is as outlined in Figure 1.

Figure 1. Methodological approach for the analysis of multi-component groups from a single emission sample.



Results and Discussion

This approach has been used successfully in the simultaneous analysis of these component classes in over 100 emission and 50 ambient air samples. By appropriate use of purification procedures and reduced final extract volumes for analysis, there is minimal loss of method detection limits compared with standard analytical procedures. Typical detection limits normally achieved using this approach are listed in Table 1.

Table 1. Method detection limits for multi-component groups in stack gas emissions and ambient air.

Multi-component Group	Method Detection Limit	
	Stack Emissions	Ambient Air
PCDDs/PCDFs	0.001-0.005 ng m ⁻³ (TCDD)	0.001-0.005 pg m ⁻³ (TCDD)
PCBs	0.02-0.1 ng m ⁻³ (co-planar)	0.02-0.1 pg m ⁻³ (co-planar)
PAHs	0.002-0.01 µg m ⁻³	0.002-0.01 ng m ⁻³
OPPs	0.1-0.5 µg m ⁻³	0.1-0.5 ng m ⁻³
OCPs	0.02-0.1 µg m ⁻³	0.02-0.1 ng m ⁻³

An important aspect of the development of this methodology, and as part of on going quality assurance procedures, has been the analysis of a series of matrix spike samples. Matrix spikes are carried out by adding native material to either XAD-2 resin (for emissions) or a mixture of PUF/XAD-2 resin (for ambient air) and extracting and analysing the sample as detailed previously. The results of a number of matrix spike samples are reported for PCDDs and PCDFs in Table 2.

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Table 2. Matrix spike recovery data for PCDDs and PCDFs.

PCDD/PCDF	Stack Emissions (n = 13)		Ambient Air (n = 8)	
	Range, %	Mean, %	Range, %	Mean, %
2378-TCDD	67-95	86	68-83	77
2378-TCDF	73-102	91	77-85	82
12378-PeCDD	76-107	90	71-80	76
12378-PeCDF	76-95	86	69-82	73
123478-HxCDD	92-120	95	72-86	79
123478-HxCDF	67-99	86	65-87	77
1234678-HpCDD	85-129	100	72-89	78
1234678-HpCDF	68-110	86	46-115	90
OCDD	76-118	101	51-119	93
OCDF	75-145	104	62-90	75

Similarly, mean matrix spike recovery data for the PCBs were in the range 69-120% (stack emission) and 81-122% (ambient air), for PAHs in the range 92-115% (emission) and 85-125 (air), for OPPs in the range 94-118% (emission) and 77-144% (air) and for OCPs in the range 75-103 (emission) and 78-109% (air).

This method can also be applied to the determination of other toxic organic contaminants known to occur in emissions from stationary sources, most notably the polychlorinated naphthalenes and the chlorobenzenes.

The basis of this multi-analyte approach is the successful combination and application of advanced analytical and instrumental techniques. In particular, this necessitates:

- Use of appropriately labelled field and method clean up spikes, and the use of other surrogate standards at specified steps in the method
- Optimisation of all purification procedures so as to achieve efficient separation of component classes and to allow for reduced final extract volumes for analysis.

The method described uses established multi-media sampling systems to allow for the efficient collection of a wide range of trace organic contaminants found in stack emissions and ambient air. The use of advanced analytical techniques provides for the measurement of a range of multi-component groups of compounds to limits of detection that are appropriate for their relative environmental significance, and with increased levels of quality assurance. In addition, the use of combined sampling and analytical techniques provides significant cost savings over existing methods. This approach has important applications in the assessment of the impacts of a wide range of toxic organic contaminants in stack emissions, in determining their fate in the atmosphere and in the assessment of air quality. The method is now being successfully applied in field studies in the assessment of the impact of emissions on surrounding areas.