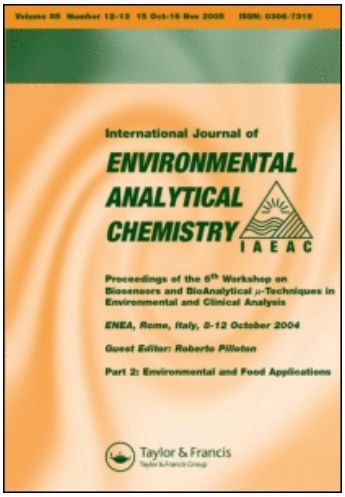

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Description of a Method for Automated Determination of Organic Pollutants in Water†

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A method for automated determination of 73 organic pollutants in water is described. The compounds, which are key representatives for different types of pollutants are determined in two chromatographic runs. 11 halogenated aliphatic hydrocarbons are determined using capillary GC equipped with electron capture detector. The remaining pollutants, representing both basic/neutral and acidic compounds are determined by using GC/MS combined with an automated search computer program. The majority of the compounds have a limit of quantitation at 1 μg/l or lower. The precision of the GC method is in the range of 1.8% to 4.3%, with an average of 3.2%. The precision for compounds determined by GC/MS is in the range of 1% to 38%, with an average of 14%.

So far 30 water samples representing both polluted fjord areas as well as effluents from municipal treatment plants, refineries, petrochemical industries and metallurgic industries have been analysed. The method has been found to be an interesting alternative to traditional methods for monitoring water quality, and has demonstrated its potential both as a screening method for detecting "hot spots" as well as for routine monitoring of specific hazardous compounds.

KEY WORDS: Halogenated aliphatic hydrocarbons, capillary GC, electron capture detector capillary GC/MS, automated search, computer programme.

INTRODUCTION

During recent years more than 2000 organic compounds have been reported to be present in natural waters, ground water, drinking

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water, and industrial effluents.[1] Many of these compounds are anthropogenic pollutants either known or suspected to be harmful to humans or to ecosystems. Several methods of different sophistication exist for monitoring organic pollutants. These range from the simplest pH and turbidity measurements via group type analyses (total organic chlorine, phenols etc.) to highly sophisticated GC/MS, MS/MS or HPLC/MS methods either for the determination of selected priority pollutants or for total evaluation of all compounds present. To get sufficient information to perform an environmental impact evaluation of the effluents it is often necessary to use the most sophisticated methods. Traditionally such methods are, however very time consuming and expensive and therefore not suited for routine monitoring.

During the last years methods for automated multitarget compound analysis have been published. Of great interest are those adapted for GC/MS, where the compounds are automatically determined using a computer program which compares retention time as well as mass spectrum of candidate compounds to information of the target compounds stored in the computer library. High degree of automation allows determination of a large number of target compounds at reasonable cost. Especially in U.S. great efforts have been made in developing well suited computer programs, and reports are published where these programs have been adapted to analysis of the 114 organic U.S. priority pollutants.[2,3,4]

At our institute we have also focused interest on multitarget compound analysis. In this paper we describe an automated GC and GC/MS method for determination of 73 organic waterpollutants of special interest in Norway. The method is discussed in terms of time-effectiveness, precision, sensitivity and specificity, and its application to environmental samples are demonstrated.

EXPERIMENTAL

The target compounds

The 73 organic target compounds are listed in Table I. Some of the compounds are a group of isomers rather than one specific compound. The compounds on the list have been selected jointly by the Norwegian State Pollution Control Authorities and our institute.[5]

TABLE I

Precision, limit of quantitation and frequence of appearance of the 73 target compounds. Frequence of appearance is based on analyses of 28 samples representing polluted fjord areas and effluents from refineries, petrochemical industry, metallurgi industry and municipal waste water treatment plants.

Name	Precision (RSD)	Limit of quantitation (μg/l)	Frequence of appearance (%)
Mono- and bicyclic aromatic hycrocarbons:			
Benzene	27	50	32
Toluene	13	130	46
Ethylbenzene	23	5	39
m-/p-Xylene	19	10	53
o-Xylene	25	5	53
Styrene	29	1	46
Napthtalene	13	1	71
1-Methylnapthtalene	18	1	68
2-Methylnapthtalene	24	1	62
2, 3-Dimethylnaphthalene	8	11	50
2, 3, 5-Trimethylnaphthalene	4	1	61
Biphenyl	5	1	57
Polycyclic aromatic hydrocarbons:			
Dibenzofurane	3	1	43
Phenanthrene	10	1	53
Dibenzothiophene	12	1	28
Pyrene	6	1	53
Fluoranthene	3	1	46
Benzo(b)fluorene	6	1	25
Benzo(a)anthracene	9	1	46
Crysene/Triphenylene	1	1	39
Benzo(e)pyrene	6	1	25
Benzo(a)pyrene	29	1	25
Indeno(1, 2, 3-c, d)pyrene	12	1	18
Benzo(g, h, i)perylene	12	1	14
Benzo(b, j, k)fluoranthene	11	2	21
Chlorinated aromatic hydrocarbons:			
Chlorobenzene	21	1	7
1, 3-Dichlorobenzene	8	1	21
1, 4-Dichlorobenzene	9	1	46
1, 2-Dichlorobenzene	7	1	25
1, 2, 4-Trichlorobenzene	10	1	25
Pentachlorobenzene	9	1	7
Hexachlorobenzene	10	1	4
Octachlorostyrene	10	1	4
Tetrachlorobiphenyls	9	2	0
Pentachlorobiphenyls	8	2	7
Hexachlorobiphenyls	12	2	0
Dichloro-p-cymene	9	1	4

Name	Precision (RSD)	Limit of quantitation (µg/l)	Frequence of appearance (%)
Halogenated aliphatic hydrocarbons:			
Dichloromethane	1.8	10	17
Chloroform	1.7	0.1	79
Bromodichloromethane	2.7	0.05	13
Dibromochloromethane	3.7	0.05	0
Bromoform	4.3	0.1	8
Tetrachloromethane	3.4	0.01	21
Trichloroethene	3.5	0.1	38
1, 1, 1-Trichloroethane	2.3	0.05	42
1, 1, 2-Trichloroethane	3.1	0.5	4
Tetrachloroethane	4.0	0.01	71
Hexachloroethane	4.0	0.01	0
Pesticides:			
Lindane	10	1	0
4, 4'-DDE	7	1	0
4, 4'-DDD	4	1	0
4, 4'-DDT	4	1	0
Phenols:			
Phenol	7	1	61
o-Cresole	38	5	71
m-/p-Cresole	25	2	71
2-Nitrophenol	20	1	11
4-Nitrophenol	17	5	0
p-Nonylphenol	38	10	68
2, 4, 6-Trichlorophenol	28	1	7
Pentachlorophenol	28	1	18
Tetrachlorogùariacol	35	5	4
Phosphate esters:			
Tri-n-bùtylphosphate	22	1	39
Triphenylphosphate	6	1	0
Tricresylphosphate	12	1	0
Phthalates:			
Dimethylphthalate	9	1	14
Diethylphthalate	8	1	39
Di-n-butylphthalate	15	5	11
Butylbenzyl phthalate	6	1	14
Di-(2-ethylhexyl)-phthalate	10	5	75
Adiphates:			
Di-(2-ethylhexyl)-adiphate	15	1	32
Aromatic nitrogen compounds:			
Nitrobenzene	8	1	0
Diphenylamine	32	1	21
Ethers:			
Dioxane	32	5	36

The selection is based on toxicity, mutagenicity, accumulation potential in organisms, as well as frequence of appearance in Norwegian environmental samples. In addition, some of the compounds have simply been selected due to a wish of a better evaluation of their presence in the environment. Only compounds which are gas chromatographically detectable without prior derivatization have been selected.

The 73 compounds are analysed in two chromatographic runs; 11 volatile halogenated aliphatics by gas chromatography with electron capture detector and the remaining 62 compounds by computerized gas chromatography/mass spectrometry.

Gas chromatographic analysis

The analysis is based on a method described by Eklund *et al.*[6] 100 ml water is extracted with 5 ml distilled n-pentane containing bromotrichloromethane as internal standard. 3 ml of the n-pentane extract is shaken with 3 ml concentrated sulphuric acid. After centrifugation 1 ml of the n-pentane phase is transferred to an auto sampler vial. 2 μl of the sample is injected splitless on a Hewlett Packard 5730A gas chromatograph equipped with a Hewlett Packard 3388A integrator, Hewlett Packard 7671A auto sampler, and a Ni^{63} electron capture detector. The gas chromatograph is supplied with a 50 m SE-54 chemically bonded glass capillary column (Jaeggi, Switzerland) with 0.15 μm film thickness. Hydrogen is used as carrier gas (15 psi inlet pressure) and argon with 5% methane as make-up gas (40 ml/min). The injector temperature is held at 200°C and the detector at 250°C. The oven is initially held at 25°C for 4 min. The temperature is thereafter raised to 100°C by 4°C per min.

The identification of the different compounds is based on relative retention time, and the quantitation is performed from multi level response factors. The response factor is determined by spiking water samples with varying amounts of the standard compounds.

Gas chromatographic/mass spectrometric analysis

1 liter or 0.1 liter of water is spiked with 10 μg deuterated internal standards (toluene-d_8, napthtalene-d_{10}, biphenyl-d_{10}, phenanthrene-d_{10}, pyrene-d_{10}, crysene-d_{12}, and phenol-d_6). Base-neutral com-

pounds are extracted with three sequential 35 ml aliquots of distilled dichloromethane in a separatory funnel after adjusting the water to pH 11 with 5M sodium hydroxide. The water sample is thereafter acidified to pH 2 using 5M sulphuric acid and the acidic priority pollutants are extracted with three sequential aliquots of 35 ml distilled dichloromethane. The six dichloromethane extracts are combined, dried with sodium sulphate and the volume is reduced to 5 ml at 30°C using a modified Kuderna–Danish distillation. The extract is further reduced to 1.0 ml under a gentle stream of nitrogen at 30°C.

The extracts are analysed using a Finnigan 9610 gas chromatograph interfaced to a Finnigan 4023 quadrupole mass spectrometer and an Incos 2300 data system with a 96 megabyte CDC disk drive. The gas chromatograph is supplied with a computer controlled Varian 80000 auto sampler. Mass spectra is recorded with 1 scan per 0.6 sec in full scan mode (35–400 amu). The mass spectrometer is operated in the electron impact mode at 70 eV and tuned with FC43 so that the intensity of m/z 131 and m/z 219 is equal. The analysis is performed using a 30 m DB-5 fused silica capillary column with 0.25 μm film thickness (J & W Scientific, Inc.). The column is introduced directly into the ion chamber keeping the injector temperature at 280°C, interface oven at 240°C, and the ion chamber at 250°C. The oven is initially held at 30°C for 5 min before quickly raising the temperature to 70°C. Thereafter the temperature is raised by 4°C per min to 300°C and kept there for 10 minutes.

Automated identification and quantitation of the target compounds are performed using a modified version of Finnigan MAT's Organics-In-Water Analyzer software for targer compound analysis.[2] Each compound has its own library entry with a simplified mass spectrum containing three characteristic masses, name of compound, entry number, retention time, relative retention time, molecular weight, formula and single mass for quantitation. Unknown samples are analysed by reversed library search within a given retention window (50 sec) centered around the theoretic relative retention time of the target compound versus the deuterated internal standard. The target compound is positively identified if the mass spectrum of a given scan within the retention window match with that in the library (match index (FIT) > 900).

The quantitation is based on multi level response factors covering both differences in extraction behaviour, volatility and GC/MS response of the compounds and of the deuterated internal standards. 1 liter pentane washed water is spiked with 10 μg deuterated internal standards and normally 1, 5, 25, and 100 μg of the different target compounds. Calibration curves are automatically calculated and stored on the disk, and quantitation is based on area of ion chromatogram of one specific mass for each compound.

The report consists of three parts, (i) a reconstructed ion chromatogram, (ii) a report with name and amount of compounds arranged according to chemical formula, (iii) a reversed search status report containing the data needed to evaluate the results, i.e. found retention time versus theoretic retention time and library matching.

RESULTS AND DISCUSSION

Method evaluation

The analytical method has been tested with respect to, precision, sensitivity and specificity on both standard mixtures and samples from industrial and municipal wastewater.

Precision: Precision describes the degree to which data generated form replicate or repetitive measurements differ from one another.[7] Precision in determination of halogenated aliphatic hydrocarbons was determined from 4 replicate samples spiked with standards at concentrations 100 times above the limit of quantitation. The obtained precisions were in the range of 1.8% to 4.3% with an average of 3.2%. Precision of the GC/MS method was also calculated using 4 replicates but at four different levels of concentration; 1, 5, (10), 25 and 100 μg/l water. The values ranged from 1% to 38% with an average of 14%. Highest standard deviations was found for the monoaromatic hydrocarbons, the phenols and diphenylamine. (see Table I).

Sensitivity: The sensitivity of the method was determined from water samples spiked with the target compounds, and expressed in terms of limit of detection (LOD) and limit of quantitation (LOQ). According to the ACS Committee on Environmental Improvements[8] the minimum criterion for LOD and LOQ should be 3σ and 10σ

above the measured average blank value, respectively. If the compounds are not found in the field blanks the LOD and LOQ should be 3σ and 10σ above the noise level, respectively.

According to these definitions 56 of the target compounds have both LOD and LOQ below 1 μg/l (see Table I). For practical reasons the LOQ of all these compounds, except the halogenated aliphatic hydrocarbons is set to 1 μg/l. Most of the halogenated aliphatic hydrcarbons have significantly lower LOQ. Highest LOQ is obtained for phenols (1–15 μg/l), monoaromatic hydrocarbons (5–130 μg/l), and phtalates (5 μg/l). For comparisons, the U.S. Environmental Protection Agency have suggested 10 μg/l as a reasonable LOQ level in industrial effluents.[4] Compounds present in concentrations below LOQ but above LOD are not quantitated. They are reported as found, but in amounts below LOQ. The LOD will vary dependent on amounts present in the blank run, but is generally one order of magnitude below LOQ.

Specificity: The specificity might be defined as to which degree the mean value of the measurements is due to the substance to be determined and not to other substances that may be present in the sample being analysed.[9] This aspect has been investigated by analyzing a series of environmental samples representing both municipal waste water and discharge water from refineries and different chemical plants. Results obtained using the automated identification and quantitation program were compared to results obtained by manual processing. Generally 10 to 30 of the target compounds were found in each sample and the chromatograms were often very complex containing a great number of more or less resolved components. All compounds have still been correctly identified and quantified using the automated procedure. Our experience so far is that as long as the amount of the target components are above the LOD the components are correctly identified independent of complexity of the sample. Even components totally masked by other components are correctly identified. This is in agreement with results from previous investigations using automated software programs for identification of the U.S. priority pollutants. Statistical analyses of more than 4500 data points revealed only 0.13% false-positive and 0.04% false-negative computer identifications at a concentration above 10 ppb using a computer program from Radian Corporation.[4]

Application to environmental samples

The philosophy of the described method is that it shall serve as a screening method for detecting "hot spots" as well as a tool for a better evaluation of the general water quality of our country. At present we have investigated about 30 different environmental samples representing polluted fjord areas as well as effluents from refineries, petrochemical industry, metallurgic industry, and municipal waste water treatment plants. Several of these samples have also been manually processed for total characterization. In those cases where other types of doubtful chemicals are detected there are also substantial amounts and numbers of target compounds present, indicating a "hot spot" which should be further investigated. The results from these analyses have already given us a great deal of new information and the analytical reports will in the future provide an excellent data-base for the evaluation of which types of effluents that need further investigations. As the amount of information and knowledge increases we will also get further insight in which compounds that need further attention, whether there are components which are so infrequently found that they can be removed from the list and whether new compounds should be added.

Although our data are limited, the results from the first 30 samples already give an indication of which pollutants that are most frequently present in important industrial effluents. Not surprisingly the most frequent compounds are the mono and bicyclic aromatic hydrocarbons, cresols, di(2-ethylhexyl)phtalate, chloroform and tetrachloroethene. From Table I we see that these compounds are found in more than 60 percent of the investigated samples. More detailed lists of frequence of appearance in effluents from different industries as well as from contaminated fjord areas will be published later.

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