Completely Automated System for Determining Halogenated Organic Compounds by Multisyringe Flow Injection Analysis

3 AUTHORS, INCLUDING:

Fernando Maya
University of the Balearic Islands
46 PUBLICATIONS   **389** CITATIONS

SEE PROFILE

Víctor Cerdà
University of the Balearic Islands
1,373 PUBLICATIONS   **5,758** CITATIONS

SEE PROFILE

Completely Automated System for Determining Halogenated Organic Compounds by Multisyringe Flow Injection Analysis

Fernando Maya, José Manuel Estela, and Víctor Cerdà*

Department of Chemistry, Faculty of Sciences, University of the Balearic Islands, Carretera de Valldemossa km 7.5, E-07122 Palma de Mallorca, Illes Balears, Spain

A new, multisyringe flow injection setup was designed to develop the first completely automated flow methodology for the expeditious, accurate in-line determination of halogenated organic compounds (HOCs) in water. The target compounds are preconcentrated and isolated by solid-phase extraction. Following elution, previously organically bound halogens are released as free hydrogen halides by the combined action of UV light and a chemical oxidant for their subsequent spectrophotometric determination by reaction with $Hg(SCN)_2$ and Fe^{3+}. Optimizing the major hydrodynamic and chemical variables resulted in improved performance. Recovery of various HOCs was assessed, and potential interferents were examined. Under the selected operating conditions, the proposed method exhibits variable analytical performance depending on the particular sample volume used (e.g., a sample volume of 5 mL provides a linear working range of $140-2000\ \mu g\ L^{-1}$, a LOD of $100\ \mu g\ L^{-1}$, and a throughput of 9 samples h^{-1}). The method was successfully used to determine total adsorbable organic halogens (AOX) in well water and leachates, and the results validated against an AOX reference method. The role of the proposed system in the environmental analytical field is critically discussed.

Analytical methodologies for determining group parameters facilitate expeditious assessment of water quality.[1] The family of HOCs (see abbreviation list in Table 1) is vast and heterogeneous. A complete study of all potentially present HOCs in a concrete sample is an enormous effort. Instead, HOCs are usually determined jointly as a group parameter, which is one of the keys to assessing water quality.[2]

HOCs can come from both natural[3–5] and anthropogenic sources. The massive industrial production of HOCs has been the origin of many environmental problems. In fact, HOCs are

Table 1. List of Abbreviations

abbreviation	description
HOCs	halogenated organic compounds
OCs	nonhalogenated organic compounds
X^-	inorganic halides
HX	hydrogen halides
AOX	adsorbable organic halogens
EOX	extractable organic halogens
TOCl	total organic chloride
TOBr	total organic bromide
TOI	total organic iodide
OrgCl$^-$	Cl^-, Br^-, and I^- ions released from HOCs
DOC	dissolved organic carbon

formed in the synthesis of a variety of products (e.g., pesticides, disinfectants)[6] and in the manufacture of the most extensively used products worldwide (e.g., plastics, paper, dyes).[7] In addition, HOCs can be generated as byproduct in waters containing large amounts of OCs and X^- ions (e.g., hospital wastewater, industrial effluents).[8,9]

Most available procedures for determining HOCs as a whole involve three main stages, namely: enrichment and concomitant isolation of HOCs from the matrix of the sample; mineralization procedure of HOCs, with release of CO_2 and free HX; and quantitation of the previously released HX. The most widely accepted standard methodology for the group determination of HOCs is based on their adsorption in activated charcoal, followed by pyrolysis and coulometric titration; the result is called the "AOX group parameter".[10] There are, however, alternative analytical methodologies for this purpose including the (a) organic solvent extractable organic halogens (EOX);[11] (b) the TOCl determination by resin sorption in combination with particle induced X-ray emission spectroscopy;[12] (c) the differential determination of AOX as TOCl, TOBr, and TOI with ion chromatographic rather than

* To whom correspondence should be addressed. Tel.: +34 971 173261. Fax +34 971 173426. E-mail: victor.cerda@uib.es.

(1) Baena, J. R.; Valcárcel, M. *Trends Anal. Chem.* **2003**, *22*, 641.
(2) Maximova, N.; Dahl, O. *Chem. Soc. Rev.* **2007**, *36*, 1323.
(3) Asplund, G.; Grimvall, A.; Pettersson, C. *Sci. Total Environ.* **1989**, *81*, 239.
(4) Verhagen, F. J. M.; Swarts, H. J.; Wunberg, J.B.P.A.; Field, J. A. *Chemosphere* **1998**, *37*, 2091.
(5) Reddy, C. M.; Xu, L.; O'Neil, G. W.; Nelson, R. K.; Eglinton, T. I.; Faulkner, D. J.; Norstrom, R.; Ross, P. S.; Tittlemier, S. A. *Environ. Sci. Technol.* **2004**, *38*, 1992.

(6) Barceló, D.; Petrovic, M. *Trends Anal. Chem.* **2007**, *26*, 2.
(7) Lacorte, S.; Latorre, A.; Barceló, D.; Rigor, A.; Malmqvist, A.; Welander, T. *Trends Anal. Chem.* **2003**, *22*, 725.
(8) Emmanuel, E.; Keck, G.; Blanchard, J.; Vermande, P.; Perrodin, Y. *Environ. Int.* **2004**, *30*, 891.
(9) Baycan, N.; Thomanetz, E.; Sengül, F. *J. Hazard. Mater.* **2007**, *143*, 171.
(10) European Standard EN 1485, Water-quality determination of adsorbable organically bound halogens. 1996.
(11) Contreras Lopez, M. C. *Environ. Int.* **2003**, *28*, 751.
(12) Hemming, J.; Holmbom, B.; Jämström, S.; Vuorinen, K. *Chemosphere* **1984**, *13*, 513.

coulometric detection;[13] (d) the manual determination of AOX by resin sorption followed by microwave digestion of the resin and spectrophotometric detection;[14] (e) the determination of AOX by atomic emission spectrometry (AES) rather than coulometry;[15] (f) the AOX determination using thermal desorption rather than pyrolysis prior to AES detection;[16] and (g) an automated batch determination method involving flow injection preconcentration of AOX in activated charcoal, followed by automatic discharge of the charcoal into a pyrolytic wave and AES detection.[17] To the best of our knowledge, no existing methodology for this purpose relies on an in-line continuous procedure for the simple, rapid determination of HOCs in a completely automated manner, even though it might substantially surpass existing choices in performance. Various flow injection techniques[18–20] have proved highly effective toward automating analytical procedures. One such technique is multisyringe flow injection (MSFI),[21–24] where fluids are driven across a flow manifold by a multisyringe buret (MS). An MS with 4 syringes affords up to 32 different injection modes, thereby vastly expanding the flexibility of automated microfluid handling.

In this work, the MSFI technique was used for the automated in-line determination of HOCs as a group parameter. To this end, organic compounds were preconcentrated and isolated from their sample matrix by solid-phase extraction (SPE). The solid phase was rinsed with a nitrate solution in order to effect competitive desorption of interfering X^- ions, the target compounds being eluted with an organic solvent/water mixture. The eluate was mixed with a chemical oxidant (persulfate ion, $S_2O_8^{2-}$) and irradiated with UV light. HOCs were thus oxidized and released CO_2, which was removed with a debubbler, and HX as a result. Released HX were then reacted with $Hg(SCN)_2$ to obtain free SCN^- ions, which were concomitantly reacted with Fe^{3+} to obtain a deeply colored coordination complex. Monitoring the absorbance of the complex at 480 nm allowed the analytical signal for released Cl^-, Br^-, and I^- ions, measured as micrograms of $OrgCl^-$ L^{-1}, to be obtained.

The $X^-/Hg(SCN)_2/Fe^{3+}$ reaction system[25] has proved efficient for determining X^- ions in both aqueous[26–28] and polar organic

media.[9] In this work, the ions were determined in an aqueous/organic mixed medium. We chose to use this reaction system on the grounds of its simplicity and also for comparison with the detection method typically used by AOX standard analyzers, which afford the simultaneous determination of Cl^-, Br^-, and I^- ions released from HOCs. *Mercury(II) thiocyanate is very toxic by inhalation, in contact with skin, and if swallowed. It is environmentally hazardous and highly toxic to aquatic organisms. Protective gear should be used at all times and the waste products handled as hazardous chemical waste.*

The proposed MSFI setup was initially operated as a sequential injection (SI)[19] preconcentration system; however, once the eluent was released, it was switched to a forward flow mode as in classical flow injection[18] systems.

In summary, the aim of this work was to explore the use of the MSFI technique for improving existing methodologies for the determination of HOCs as a group parameter and to develop the first approach to date to the accurate, expeditious assessment of HOCs. The applicability of the proposed system is reflected in its intrinsic features (adsorption−UV irradiation−oxidation−spectrophotometric detection). This is the first reported method for the completely automated in-line determination of the parameter AOX.

EXPERIMENTAL SECTION

Chemicals and Sorbents. All chemicals were reagent-grade and used without further purification. Millipore-quality water was used to prepare solutions. The reagent stock solutions used included the following: (a) 2 mmol L^{-1} mercury(II) thiocyanate (0.063 g of $Hg(SCN)_2$ (Fluka, Deisenhofen, Germany) in 0.1 L of a 99:1 (v/v) water−methanol mixture), which was prepared on a daily basis under gentle heating in a steam bath; (b) 0.3 mol L^{-1} iron(III) (12.12 g of $Fe(NO_3)_3 \cdot 9H_2O$ (Fluka) in 0.1 L of 1.3 mol L^{-1} HNO_3); (c) sodium persulfate (5 g of $Na_2S_2O_8$, Fluka, in 0.1 L of 0.13 mol L^{-1} HNO_3); and (d) sodium nitrate (0.2 g of $NaNO_3$, Fluka, in 0.1 L of 0.13 mol L^{-1} HNO_3). The eluents used were methanol, ethanol, 2-propanol, and acetonitrile (all from Panreac, Castellar del Valles, Spain). HOC stock standard solutions containing 1 g of $OrgCl^-$ L^{-1} were prepared by dissolving 0.362 g of 4-chlorophenol (Aldrich, Deisenhofen, Germany) in 0.1 L of 0.01 mol L^{-1} NaOH. The other HOCs studied, which are referred to in subsequent sections and were all obtained from Aldrich, were also dissolved in 0.01 mol L^{-1} NaOH or, if necessary, in the minimum amount of methanol. Working-strength solutions were prepared by appropriate dilution of the stocks and acidified to pH <2 with HNO_3. Various commercial disinfectants including Preventol BP and Preventol CMK (Lanxess), Zotal D (Zotal), and Cresovex S (SP Veterinaria) were also studied. These products contain one or more HOCs in their composition, the amount of each component being stated by the manufacturer on its commercial container. Preventol BP and Preventol CMK are solid chlorinated phenols, so they were dissolved and diluted to appropriate concentrations. Zotal D and Cresovex S are commercial solutions containing 2.65 and 18.3 g of $OrgCl^-$ L^{-1}, so they were directly diluted to appropriate concentrations. The solid reversed-phase materials used to extract HOCs were Chromabond HR-P.AOX (a modified poly(styrenedivinylbenzene) resin from Macherey-Nagel); C18-octadecyl-, SDB-XC-poly(styrenedivinylbenzene)- and SDB-RPS- poly(styrenedivinylbenzene)-modified sorbent disks (Empore 3M, St Paul, MN).

(13) Oleksy-Frenzel, J.; Wischnack, S.; Jekel, M. *Fresenius' J. Anal. Chem.* **2000**, *366*, 89.
(14) Macherey-Nagel GmbH & Co. KG, Article 985 007, 2007.
(15) Rodríguez, J.; Pereiro, R.; Sanz-Medel, A. *Anal. At. Spectrom.* **1998**, *13*, 911.
(16) Lehnert, H.; Twiehaus, T.; Riepling, D.; Buschner, W.; Cammann, K. *Analyst* **1998**, *123*, 637.
(17) Twiehaus, T.; Evers, S.; Buscher, W.; Cammann, K. *Fresenius' J. Anal. Chem.* **2001**, *371*, 614.
(18) Ruzicka, J.; Hansen, E. H. *Anal. Chim. Acta* **1975**, *78*, 145.
(19) Ruzicka, J.; Marshall, G. D. *Anal. Chim. Acta* **1990**, *237*, 329.
(20) Rocha, F. R. P.; Reis, B. F.; Zagatto, E. A. G.; Lima, J.F.L.C.; Lapa, R. A. S.; Santos, J. L. M. *Anal. Chim. Acta* **2002**, *468*, 119.
(21) Cerdà, V.; Estela, J. M.; Forteza, R.; Cladera, A.; Becerra, E.; Altamira, P.; Sitjar, P. *Talanta* **1999**, *50*, 695.
(22) Miró, M.; Cerdà, V.; Estela, J. M. *Trends Anal. Chem.* **2002**, *21*, 199.
(23) Segundo, M. A.; Magalhaes, L. M. *Anal. Sci.* **2006**, *22*, 3.
(24) Horstkotte, B.; Elsholz, O.; Cerdà, V. *J. Flow Injection Anal.* **2005**, *22*, 99.
(25) Zall, D. M.; Fisher, D.; Garner, M. Q. *Anal. Chem.* **1956**, *28*, 1665.
(26) Ruzicka, J.; Stewart, J. W. B.; Zagatto, E. A. G. *Anal. Chim. Acta* **1976**, *81*, 387.
(27) Silva, C. R.; Vieira, H. J.; Canaes, L. S.; Nóbrega, J. A.; Fatibello-Filho, O. *Talanta* **2005**, *65*, 965.
(28) Maya, F.; Estela, J. M.; Cerdà, V. *Talanta* **2008**, *74*, 1534.
(29) Drug, F. J.; Pessenda, L. C. R.; Zagatto, E. A. G.; Jacintho, A. O.; Reis, B. F. *Anal. Chim. Acta* **1981**, *130*, 409.
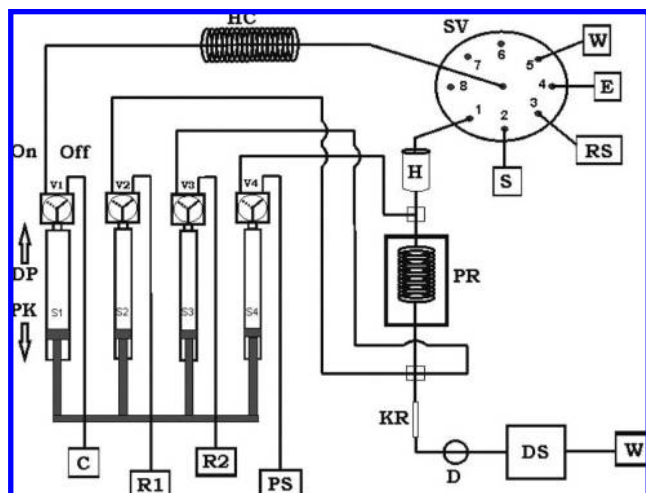
Figure 1. Schematic depiction of the proposed MSFI setup for the determination of HOCs. S1–S4 syringes, V1–V4 solenoid valves, C carrier reservoir, R1 $Hg(SCN)_2$ solution reservoir, R2 Fe^{3+} solution reservoir, PS $Na_2S_2O_8$ solution reservoir, DP dispense solutions, PK pickup solutions, Off normally open position of the solenoid valves (syringes connected with the reservoirs), On normally closed position of the solenoid valves (syringes connected to the flow network), HC holding coil, SV selection valve, S sample solution reservoir, RS rinsing solution reservoir, E eluent solution reservoir, W waste reservoir, H flow through sorbent holder, PR photoreactor, KR knotted reactor, D debubbler, and DS detection system.

Standard Reference Method. The proposed methodology was validated by using a suitable reference method for determining HOCs as a group parameter. Concretely; a Euroglas (Delft, The Netherlands) ECS 1200 AOX analyzer was used to implement the EN 1485[10] European Standard Method for AOX determination, which is similar to EPA Method 1650 for Adsorbable Organic Halides by Adsorption and Coulometric Titration. Briefly, this standard method involves the following steps: samples are acidified to pH <2 with HNO_3 and stored at 4 °C. Then, an Erlenmeyer flask is supplied with 100 mL of the water sample and 50 mg of activated charcoal and shaken for 1 h, after which the charcoal is filtered through a quartz holder and rinsed with a $NaNO_3$ solution to remove X^- ions. The quartz holder containing the filtered activated charcoal is then burnt at 950 °C to release HX compounds, which are transported to a microcoulometric cell by an O_2 stream. Finally, released HX compounds are titrated by precipitation as silver halides. This method provides a linear working range of 10–300 μg of $OrgCl^-$ L^{-1}. In theory, it can tolerate a maximum amount of X^- and DOC of 1000 and 100 mg L^{-1}, respectively; however, real measurements provided a maximum tolerated levels of only 600 mg L^{-1} X^-.

Instrumentation and Software. Figure 1 depicts the proposed flow system. A multisyringe automatic buret (MS) from Crison (Alella, Barcelona, Spain) was used to drive the liquid to the flow network. The buret was equipped with four syringes (S1–S4), and each syringe is mounted between a common metallic bar and its own three-way solenoid valve (V1–V4; N-Research, West Caldwell, NJ); as a result, the four syringes were operated simultaneously. Depending on the position of the solenoid valves, the fluids contained in syringes were loaded (PK, pickup) or dispensed (DP, dispense) to the flow network (on) or the reservoirs (off). Syringe S1 (10 mL) acted as a flow carrier and was connected to an eight-port selection valve (SV) from
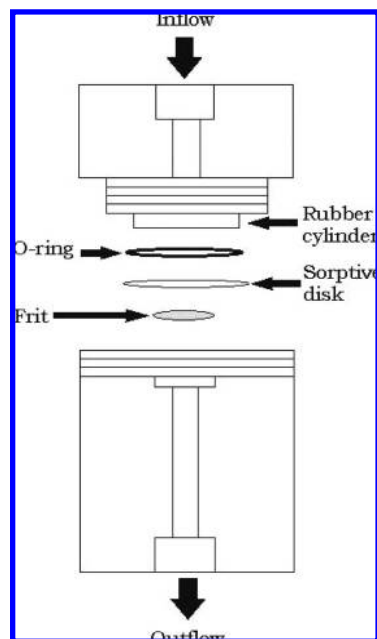

Figure 2. Schematic depiction of the device used for in-line solid-phase extraction with sorbent disks 9 mm in diameter.

Crison, which allowed the sequential automated microfluid handling of the sample (S), rinsing solution (RS), and eluent (E). The other three syringes, however, were used for injection of their respective solutions in the forward flow mode, thereby avoiding the typical mixing problems of sequential injection systems. S2 (5 mL) and S3 (5 mL) contained $Hg(SCN)_2$ and Fe^{3+} solutions, respectively, and S4 (2.5 mL) was filled with $Na_2S_2O_8$ solution.

Miniaturized solid-phase extraction was performed in a laboratory-made holder (H) shown in Figure 2. The holder was a Perspex cylindrical block (2 cm × long 1.3 cm i.d.) with a central cavity in which an extraction disk 9 mm in diameter was accommodated in order to pass the different fluids involved in the SPE procedure. The PR consisted of a laboratory-made wood box accommodating an 8-W mercury lamp ($\lambda_{max} = 254$ nm) with a poly(tetrafluoroethylene) (PTFE) tube 200 cm long × 0.8 mm i.d. directly wound around it. Just in the outlet of the PR, a PTFE tube knotted reactor is placed (50 cm × 0.8 mm i.d.) to facilitate the reaction product development and also with a debubbler (D, Trace Analytics, Braunschweig, Germany). All other tubing was also PTFE (0.8 mm i.d.), and merging connectors were made from poly(methyl methacrylate) (PMMA). The DS consisted of a deuterium–halogen light source (Mikropack, Ostfildern, Germany), two optical fibers 400 μm in diameter (Ocean Optics, Dunedin, FL), a 18-μL glass flow cell of 1-cm path length (Hellma, Mülheim, Germany), and a USB 2000 miniature fiber-optic spectrometer (SPM) (Ocean Optics) connected to a computer via a USB interface. We chose to use dual-wavelength spectrophotometry (480 and 700 nm) in order to minimize the Schlieren effect.[30]

Execution of the analytical protocol was computerized by using the AutoAnalysis 5.0. software package (Sciware, Palma de Mallorca, Spain). The basic program contains appropriate dynamic link libraries[31] to implement MS, SV, and SPM.

(30) Zagatto, E. A. G.; Arruda, M. A. Z.; Jacintho, A. O. *Anal. Chim. Acta* **1990**, *234*, 153.
(31) Becerra, E.; Cladera, A.; Cerdà, V. *Lab. Rob. Autom.* **1999**, *11*, 131.

Table 2. Main Steps of the AutoAnalysis 5.0 Standard Analytical Procedure for AOX Determination

step	inst	system protocol	analytical description
1		start loop A	start AOX determination protocol
2		start loop B	start preconcentration cycle
3	SV	move to position 2	connecting S1 with S reservoir
4	MS	PK 5 mL at 5 mL min^{-1} (on/off/off/off)	S loading
5	SV	move to position 1	connecting S1 with the flow network
6	MS	DP 6 mL at 3 mL min^{-1} (on/off/off/off)	preconcentration of the target species
7		end loop B	end cycle; repeat X times
8	SV	move to position 3	connecting S1 with RS reservoir
9	MS	PK 0.5 mL at 5 mL min^{-1} (on/off/off/off)	RS loading
10	SV	move to position 1	connecting S1 with the flow network
11	MS	DP 2 mL at 3 mL min^{-1} (on/off/off/off)	removing possible X^{-} residues
12	SV	move to position 4	connecting S1 with E reservoir
13	MS	PK 0.5 mL at 2 mL min^{-1} (on/off/off/off)	eluent loading
14	SV	move to position 1	connecting S1 with the flow network
15	MS	DP 1 mL at 1 mL min^{-1} (on/off/off/on)	elution and mixing with oxidant
16		wait (stop flow for 60 s)	UV oxidation
17	SPM	start reading every 0.4 s (A, 480; R, 700)	start absorbance data acquisition
18	MS	DP 2 mL at 1.5 mL min^{-1} (on/on/on/off)	analytical signal acquisition
19	SPM	stop measure	finish absorbance data acquisition
20		end loop A	determination finished; repeat X times

Analytical Procedure. Table 2 summarizes the general analytical procedure for the automated determination of HOCs as a group parameter using the MSFI technique. The procedure is based on a main cycle (loop A) that includes the steps needed for complete sample pretreatment and subsequent determination of HOCs as OrgCl^{-}. Loop A includes a subcycle (loop B) that is used to preconcentrate 5 mL of sample—the maximum volume that can be loaded into HC. Loop B can be repeated as many times as required to increase the preconcentration factor of the target compounds. Once the preconcentration cycle is completed, the procedure continues with solid-phase rinsing prior to elution of the target species. Finally, an in-line approach is also used to oxidize the target species with S$_2$O$_8^{2-}$/UV light and detect them spectrophotometrically as OrgCl^{-}.

RESULTS AND DISCUSSION

In-Line Solid-Phase Extraction. According to DIN 38409-H22, the efficiency of activated charcoal, which is the classical sorbent for HOCs, can be increased by using copolymeric poly(styrenedivinylbenzene)-modified resins.[32] We tested this material as a solid phase and assessed its HOC extraction capabilities in two different forms, namely: (a) resin (HR-P.AOX) of pore diameter 60 Å, surface area 1270 m^2 g^{-1} and average particle size 85.80 μm packed in PMMA cylinders 18 mm long × 2 mm i.d.; and (b) disks (SDB-RPS) 47 mm in diameter consisting of 90% adsorbent particles 0.5 ± 0.05 mm in width linked by 10% PTFE that were used at a maximum flow rate of 100 mL min^{-1} (the particles had a pore diameter of 60 Å, a surface area of 450 m^2 g^{-1}, and an average size of 12 μm, and a portion 9 mm in diameter of disk was placed in the holder of Figure 2, the resulting maximum flow rate in the SPE device being 4 mL min^{-1}). The sorbents were compared in terms of performance by using a solution containing 1.5 mg L^{-1} OrgCl^{-} (from 4-chlorophenol) that was eluted with a 20:80 (v/v) water—ethanol mixture. The sorption disks were found to exhibit better analytical performance in terms of blank and signal repeatability, the absence of overpressure or particle compaction, a longer useful life of the sorbent material, no carryover, and a 56% increase in peak height. We thus chose to use the sorbent in disk form and tested C18 and SDB-XC as sorbents for the solid-phase extraction of HOCs. C18 disks were found to result in poor repeatability, significant carryover, and a 43% lower peak height than SDB-RPS disks. On the other hand, SDB-XC disks retained the favorable properties of SDB-RPS disks in addition to providing improved signal repeatability and 23% higher peak height. This led us to adopt SDB-XC disks as the sorbent material for SPE.

We studied methanol, ethanol, 2-propanol, and acetonitrile as potentially effective solvents for HOCs. To this end, we used 80:20 (v/v) solvent—water mixtures to elute a volume of 5 mL of the previous 1.5 mg L^{-1} 4-chlorophenol solution. The highest recoveries under these conditions were obtained with 2-propanol, those provided by methanol and ethanol being 30 and 60% lower, respectively. Also, acetonitrile was discarded owing to its incompatibility with the postcolorimetric reaction. Finally, the optimum proportion of 2-propanol in the water—alcohol mixed eluent was found to be 60% (v/v).

Once the most suitable sorbent material and eluent were chosen, we examined the influence of the operational variables related to their use. The effect of the eluent volume was studied over the range of 0.1−1 mL and a value of 0.5 mL selected. The effects of the preconcentration and elution flow rates were both studied over the range 1−4 mL min^{-1} (see Figure 3a). The flow rate adopted was 3 mL min^{-1} for preconcentration and 1 mL min^{-1} for elution. Mass calibration was done by using the selected SPE configuration to inject sampling volumes of 1−40 mL containing an identical amount of OrgCl^{-} (4 μg). Calibration was linear over the range 1−30 mL, and 13% analyte breakthrough was obtained by using a 40-mL sample volume.

Oxidation of Halogenated Organic Compounds. Determining halogens bound to organic compounds requires their prior decomposition in order to release free hydrogen halides in solution. One easy, highly effective way of accomplishing such decomposition is by UV photooxidation,[33] which had previously

---

(32) Borsdorf, H.; Fiedler, P.; Wilke, D.; Weiβ, H. *Acta Hydrochim. Hydrobiol.* **2003**, *31*, 19.

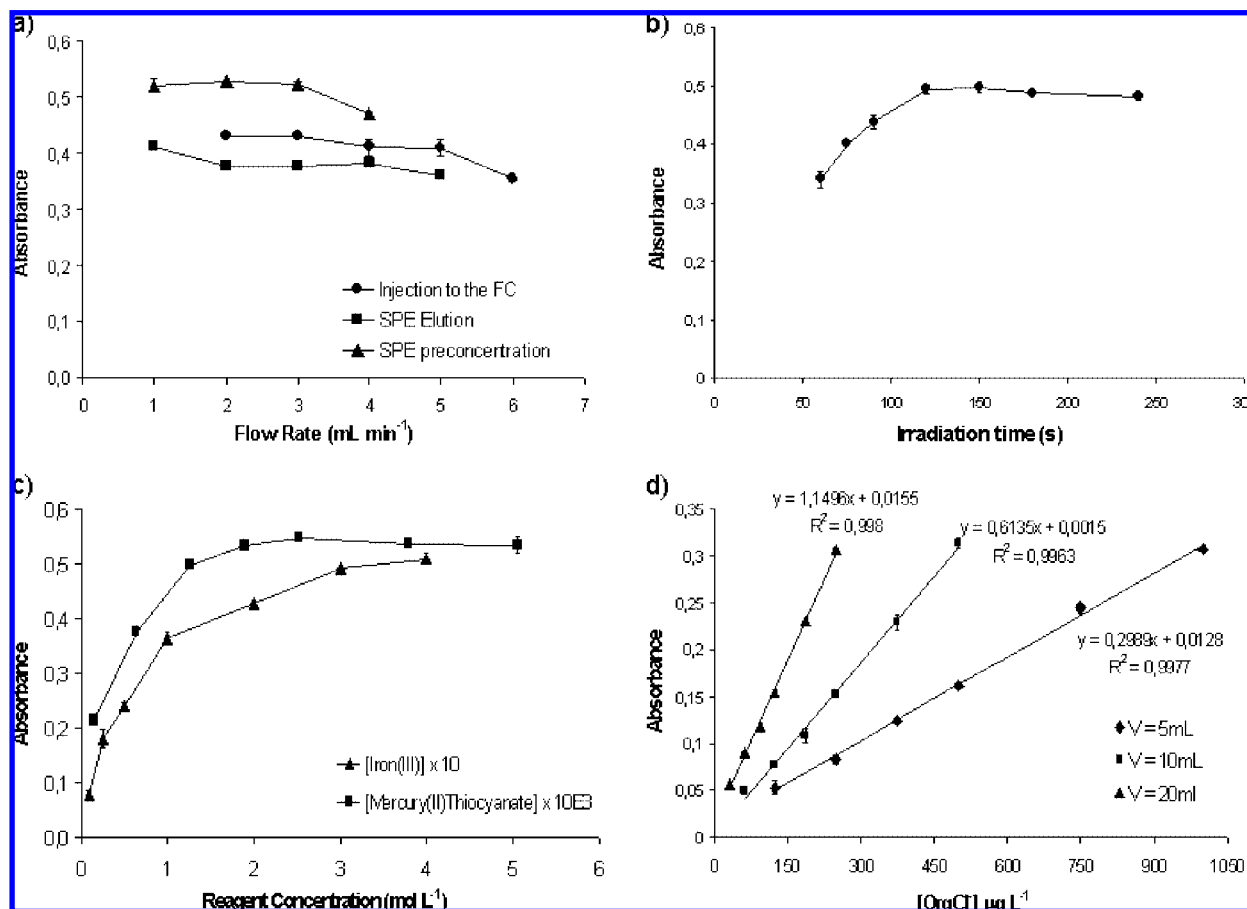(33) Golimowski, J.; Golimowska, K. *Anal. Chim. Acta* **1996**, *325*, 111.

Figure 3. Influence on the net absorbance of (a) preconcentration, elution, and injection flow rates; (b) irradiation time; (c) $Hg(SCN)_2$ and Fe^{3+} concentrations; and (d) $OrgCl^-$ concentration in three different linear dynamic ranges. Each point in the graphs represents an average value ($n = 3$) $\pm$ its standard deviation.

proved quite efficient in the flow injection determination of other parameters such as total nitrogen,[34] total phosphorus,[35] and chemical oxygen demand.[36] In this work, the oxidation potential of UV light was combined with the action of a strong chemical oxidant (viz., 50 g L^{-1} $Na_2S_2O_8$, which was quite compatible with the other chemicals used). As shown in Figure 3b, the efficiency of the photooxidation step was assessed by examining the influence of the irradiation time on the net absorbance obtained by analyzing a solution containing 1.5 mg L^{-1} $OrgCl^-$ from 4-chlorophenol (the AOX standard compound used in the EN method). An irradiation time of 120 s was selected for further testing. The choice was supported by the results obtained in the analysis of a solution containing 1.5 mg L^{-1} $OrgCl^-$ from 2,4,6-trichlorophenol (Aldrich), which is the AOX standard compound used in the EPA method.

Spectrophotometric Detection. The last step in the proposed methodology was detection of the previously released free Cl^-, Br^-, and I^- ions with the $X^-/Hg(SCN)_2/Fe^{3+}$ reaction system. In order to minimize the amount of reagents used, we examined the influence of the concentrations of $Hg(SCN)_2$ and Fe^{3+} on the

net absorbance. As can be seen from Figure 3c, best results were provided by 2×10^{-3} mol of $Hg(SCN)_2$ L^{-1} and 0.3 mol of Fe^{3+} L^{-1}, which were thus adopted for subsequent experiments. After the flowing segment containing the target species was mixed with the $Hg(SCN)_2$ and Fe^{3+} solutions in the knotted reactor, the resulting reaction plug was injected into the FC. The effect of the injection flow rate was studied over the range 2–5 mL min^{-1}, and as can be seen from Figure 3a, the best results were obtained with 3 mL min^{-1} (1.5 mL min^{-1} relative to S1).

Analytical Performance. Once the final setup was established and the influence of the main operational variables examined, the proposed methodology was assessed in terms of performance.

A sample volume of 5 mL was found to provide a linear dynamic working range of 140–2000 μg of $OrgCl^-$ L^{-1}. The limits of detection (LOD) and quantitation (LOQ) were estimated as 3 and 10 times the standard deviation of the absorbance for 10 injections of the blank (a 5×10^{-2} mol L^{-1} HNO_3 solution) and found to be 100 and 140 μg L^{-1}, respectively. The sensitivity (slope) and regression coefficient were calculated from eight day-to-day regression curves and found to be 0.2997 ± 0.0044 L μg^{-1} and 0.9973 ± 0.0010, respectively. The repeatability of the proposed method was estimated as the relative standard deviation (RSD) for 10 consecutive injections of a 1 mg of $OrgCl^-$ L^{-1} solution; under these conditions, the RSD was 2.6%. The reproducibility was calculated from the RSD of the slopes of eight day-to-day regression curves and found to be 1.7%, which is roughly 5 times

(34) Cerdà, A.; Oms, M. T.; Forteza, R.; Cerdà, V. *Analyst* **1996**, *121*, 13.
(35) Perez-Ruiz, T.; Martinez-Lozano, C.; Tomas, V.; Martin, J. *Anal. Chim. Acta* **2001**, *442*, 147.
(36) Dan, D. Z.; Sandford, R. C.; Worsfold, P. J. *Analyst* **2005**, *130*, 227.
(37) Miller, J. C.; Miller, J. N. In *Statistics for Analytical Chemistry*, 3rd ed.; Chalmers, R. A., Masson, M., Eds.; Ellis Horwood: Chichester, 2002; Chapter 3.

Table 3. Recoveries Obtained in the Analysis of Various HOCs with the Proposed System.[a]

target chemical	recovery (%)
4-chlorophenol	99
2-chlorobenzoic acid	99
3-methyl-4-chlorophenol	99
2-benzyl-4-chlorophenol	99
2-chlorophenol	98
2,4-dichlorophenol	98
2,4,6-trichlorophenol	94
pentachlorophenol	60
2-bromophenol	97
5-chloro-8-hydroxyquinoline	82
3,5-dibromosalicylic acid	98
3,5-diiodosalicylic acid	95
linuron	99
diuron	99
dieldrin	21
trichloroacetic acid	63
dichloroacetic acid	17
Preventol BP	99
Preventol CMK	98
Zotal D	98
Cresovex S	88

[a] All solutions contained 1 mg of OrgCl$^-$ L^{-1}.

better than that of AOX/EOX commercial analyzers.[2,10] The injection throughput (IT) as determined in accordance with the standard procedure was 9 samples h^{-1}. Although the operating endurance of the system was limited by the useful life of the SPE disk portion, the flow system was able to operate unattended for at least 12 h (110 injections). Consistent with the mass calibration, two additional linear working ranges obtained with 10 (LOD = 51 μg L^{-1}, LOQ = 70 μg L^{-1}, IT = 6 samples h^{-1}) and 20 mL (LOD = 27 μg L^{-1}, LOQ = 36 μg L^{-1}, IT = 3 samples h^{-1}) were established for better suitability to samples containing lower HOC levels. Figure 3d illustrates the response of the proposed system to variable sample volumes.

Response of the Proposed System to Various Halogenated Organic Compounds. We examined the response of the proposed system to various HOCs. To this end, we studied 4-chlorophenol recovery by comparing the results obtained in the direct spectrophotometric determination of 10 mg L^{-1} Cl$^-$ from NaCl (Panreac) and the in-line UV photooxidation/spectrophotometric detection of the same amount of OrgCl$^-$. The recoveries of the other HOCs studied were established by subjecting a 1 mg L^{-1} OrgCl$^-$ solution from each to the above-described in-line procedure and comparing the results with those obtained for a solution containing 1 mg L^{-1} OrgCl$^-$ from 4-chlorophenol. The recoveries thus obtained from the commercial and chemical products studied are listed in Table 3. As can be seen, most were quite good. However, some strongly persistent polyhalogenated organic compounds with very strong carbon–halogen bonds (e.g., dieldrin) were only partially oxidized and provided low recoveries; such compounds require stronger oxidation conditions (e.g., a more powerful UV lamp or a pyrolytic oven). Highly polar HOCs were also poorly recovered; as in the AOX standard method, this was a result of their being only partially retained by the SPE sorbent (viz., dichloroacetic acid).

Interference Test. The main requirement for the selective determination of OrgCl$^-$ was complete removal of X$^-$ ions from the flow network. This was accomplished by rinsing the sorbent

material with an acidified NO$_3$$^-$ solution. The effect was checked by spiking several solutions containing 100 μg of OrgCl$^-$ L^{-1} with a given amount of Cl$^-$ and subjecting them to the above-described analytical procedure. No interference was found upon addition of Cl$^-$ ion at concentrations up to 2 g L^{-1}; however, a concentration of 3 g L^{-1} Cl$^-$ increased peak height by 30%. In any case, repeating the rinsing procedure should allow water samples with higher salt loads to be analyzed, at the expense of a decreased injection throughput.

One must also consider the potential interference of nonhalogenated dissolved OCs, the presence of which can reduce SPE efficiency through partial or complete saturation of the solid support and the consequent reduction in UV oxidation efficiency. In order to study the effect of OCs on the SPE-UV oxidation in-line pretreatment, several solutions containing 100 μg of OrgCl$^-$ L^{-1} were spiked with a given amount of DOC from phenol (Aldrich), a nonhalogenated OC for which the selected SPE sorbent material has a high retention affinity. The addition of 1 g of DOC L^{-1} was found to result in no interference; however, higher concentrations decreased the analytical signal through progressive saturation of the sorbent disk portion. In conclusion, the MSFI system provides increased selectivity in the determination of AOX relative to the AOX standard method; thus, it raises the maximum tolerated levels of X$^-$ from 0.6 to 2 g L^{-1}, and those of DOC from 0.1 to 1 g L^{-1}. Samples with higher X$^-$ and DOC contents (up to 100 and 1 g L^{-1}, respectively) can be subjected to the manual cleanup pretreatment described in Appendix 1 of the EN1485 standard method (see also DIN 38409-H22).

Application and Validation of the Proposed MSFI Procedure. The accuracy of the proposed methodology was assessed by applying it to the analysis of HOCs in real samples. Samples were collected in glass bottles, acidified to pH <2 with HNO$_3$, and stored at 4 °C. None exhibited high levels of potential interferents (X$^-$ <2 g L^{-1} and DOC <0.5 g L^{-1}). Therefore, in order to validate the proposed methodology, various samples with a matrix of appropriate composition were analyzed with the AOX standard procedure (X$^-$ <0.6 g L^{-1} and DOC <0.1 g L^{-1}) and the proposed MSFI method for comparison. Using a sample volume of 20 mL with the MSFI method provided a linear dynamic range similar to that for the standard method (36–500 μg of OrgCl$^-$ L^{-1} versus 10–300 μg of OrgCl$^-$ L^{-1}).

Water samples from three different wells in the vicinity of an urban solid waste treatment plant (Mallorca, Spain) and three samples from various demolition waste treatment plant leaching dumps (Mallorca, Spain) were analyzed. The well 1, leachate 1 and leachate 2 samples (all with X$^-$ <0.6 g L^{-1} and DOC <0.1 g L^{-1}) had a suitable matrix composition for analysis with the MSFI and standard method. The results were compared via a t-test[37] that revealed the absence of differences at the 0.05 significance level. The samples leachate 3 (1 g of X$^-$ L^{-1} and 0.2 g of DOC L^{-1}), well 2 and well 3 (both with 1.5 g of X$^-$ L^{-1}) contained higher X$^-$ or DOC levels than those afforded by the standard method; however, they were satisfactorily analyzed with the MSFI method and their recoveries (102–107%) verified by addition of 4-chlorophenol. The results are shown in Table 4. In summary, the proposed MSFI system allows the accurate determination of AOX.

(38) Valcárcel, M.; Cárdenas, S. *Trends Anal. Chem.* **2005**, *24*, 67.

Table 4. Results Obtained in the Determination of Parameter AOX in Environmental Samples Using the Proposed MSFI Method and the EN-1485 Reference Method

Samples with a Matrix Suitable to Analysis with Both Methods

	added (μg L^{-1})	MSFI method ($n = 3$) found (μg L^{-1})	reference method ($n = 3$) found (μg L^{-1})
well 1	0	LOQ	
	150	148 ± 8	152 ± 2
leachate 1	0	194 ± 4	201 ± 5
leachate 2	0	228 ± 4	225 ± 3

Samples Suitable to Analysis with the MSFI Method Only

	added (μg L^{-1})	MSFI method ($n = 3$) found (μg L^{-1})	recovery (%)
well 2	0	LOQ	
	60	62 ± 6	103
well 3	0	59 ± 6	
	60	123 ± 11	107
leachate 3	0	240 ± 11	
	200	444 ± 12	102

Comparison with Other Methods of Similar Features. We compared the proposed method with others for the same purpose. No flow-based analytical methodology was seemingly reported previously, and only manual or automated batch methods for determining HOCs existed. The most similar choice for this purpose was AOX pyrolytic−coulometric commercial analyzers based on HOC sorption in activated charcoal HOCs followed by pyrolysis and coulometric detection; this approach, however, is rather different from the proposed MSFI methodology. By virtue of their intrinsic characteristics, these analysers provide a powerful mineralization procedure and better sensitivity levels than does the proposed MSFI system. On the other hand, the proposed system uses a faster, alternative in-line flow injection procedure and provides better standard deviations, in addition to markedly increased automation, robustness, cost-effectiveness, and simplicity.

Incorporation of the Proposed System into the Current Environmental Analytical Field. According to Valcárcel et al.,[38] analytical systems can be classified as vanguard analytical systems (VAS) and rearguard analytical systems (RAS). Separation techniques, which are by now widely established not only for detection, but also for identification, of HOCs,[39–41] are of the RAS type. However, vanguard systems for HOCs include various (AOX,

EOX, TOX) analyzers that are useful for determining the total amount of HOCs without identifying them and can in principle be deemed VAS. In any case, the three main features a VAS are a rapid, reliable response, simplified analytical protocols, and instrumental robustness and cost-effectiveness; therefore, the previous analyzers are redefined as RAS for HOC group parameter determination and, in consequence of this, being defenseless for the VAS zone for HOC group determinations.

The proposed MSFI constitutes a true VAS for HOC assessment inasmuch as it avoids the use of complex, time-consuming equipment to determine total parameters. As such, it can help expand the range of existing avant-garde methodologies for the nonseparative determination of HOCs in water samples, which was done here with simple analytical instrumentation including an in-line flow manifold; this can reduce costs, servicing needs, work, and time, thereby increasing operating endurance and miniaturizability.

CONCLUSIONS

Above all, the proposed MSFI methodology clearly surpasses existing analytical alternatives for the same purpose. Thus, the proposed MSFI system provides a simple and smart tool for the completely automated in-line determination of HOCs, expressed as AOX, in water. Also, it features better standard deviations, throughput, simplicity, and flexibility than pyrolytic−coulometric AOX analyzers. In addition, the ensuing methodology uses highly cost-effective, compact equipment and can be easily applied to samples containing a wide variety of matrixes.

The primary aim of this work was to develop a simple, automated vanguard methodology for the rapid group determination of HOCs without the need to assess each individual compound, which requires using more complex, expensive, and time-consuming techniques such as gas chromatography−mass spectrometry.

(39) Li, H.; Li, G.; Jen, J. *J. Chromatogr., A* **2003**, *1012*, 129.
(40) Petrovic, M.; Barceló, D.; Diaz, A.; Ventura, F. *J. Am. Soc. Mass Spectrom.* **2003**, *14*, 516.
(41) Gorka, D. F.; Pyle, S.; Titus, R. *Anal. Chem.* **1997**, *69*, 2411.