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Vapor Generation of Inorganic Anionic Species After Aqueous phase Alkylation with Trialkyloxonium Tetrafluoroborates

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Aqueous phase reaction of trialkyloxonium tetrafluoroborates, $R_3O^+BF_4^-$ ($R=Me, Et$) has been tested in the alkylation of simple inorganic anionic substrates such as halogen ions, cyanide, thiocyanate, sulphide and several oxoanions or their corresponding oxoacids. Gaseous products were separated and identified by gas chromatography mass spectrometry (GC-MS). Alkylated derivatives RI, RBr, RCl were obtained for iodide, bromide, and chloride, respectively, while for fluoride its conversion efficiency to RF is very poor. RCN and R_2S were obtained for cyanide and sulphide, while thiocyanate gives RSCN as a main reaction product with a minor amount of alkylisothiocyanate, RNCS (<7%). Among tested oxoanions only nitrites and nitrates give volatile derivatives under the form of $R-O-NO$ and $R-O-NO_2$, respectively. Reaction performed by adding $Et_3O^+BF_4^-$ in CH_2Cl_2 to aqueous sample with extraction in the organic phase of reaction products, failed to identify other less volatile reaction products. Using 2 mL sample in 4 mL reaction vial ($T = 25^\circ C$), 100 μL of 2 M $Et_3O^+BF_4^-$ and injecting 250 μL of headspace into GC-MS, detection limits (3 s) are in the range of 1–280 ng mL⁻¹. Application to determination of bromide in groundwater certified reference material (BCR-612, $252 \pm 10 \mu g kg^{-1}$ of bromide) gave results in excellent agreement with certified values. The method, being not responsive to iodate, allows the selective determination of iodide in the presence of iodate. Total iodine can be determined after reduction of iodate to iodide by $NaBH_4$. Application of the method to iodide-iodate speciation in table salt gave results in excellent agreement with parallel analysis performed by ion chromatography as a reference method.

Generation of volatile species coupled with various spectroscopic techniques represents one of the most powerful analytical tools for the determination and speciation of trace elements.^{1,2} The generation of volatile species, typically termed as vapor

generation (VG), offers the advantage of separation of the analyte from the aqueous sample, the possibility of preconcentration and speciation, and is accompanied by a significant sensitivity enhancement due to favorable features arising from the introduction of gaseous species into the detection system.

At present, several strategies for sample introduction based on VG are available. Chemical vapor generation (CVG), which is largely employed for the generation of volatile hydrides, is mainly achieved by tetrahydroborates(III) salts^{1,2} and borane complexes³ whereas CVG of volatile organometallic derivatives is typically achieved with tetraalkylborates(III)⁴ and tetraphenylborates(III).⁵ CVG of volatile hydrides and volatile alkyl derivatives includes many elements such as Ge, Sn, Pb, As, Sb, Bi, Se, Te, Hg, Cd. More recently tetrahydroborate (III) has been employed for CVG of volatile species of transition and noble metals,^{6,2} but the nature of volatile metallic species has not been identified and is still matter of debate.⁷

Electrochemical vapor generation technique (ECVG), recently reviewed by Laborda et al.,⁸ is mainly employed as a sample introduction technique of most classical hydride forming elements, As, Sb, Bi, Ge, Sn, Se, Hg, and Cd. More recently, photochemical vapor generation (PVG) has been proposed as a derivatization technique for the conversion of Se(IV) by UV irradiation in the presence of low molecular organic acids (formic, acetic, propionic and malonic acids),⁹ but subsequently PVG has been expanded to many other elements as the classical hydride forming As(III), Bi(III), Sb(III), Sn(IV), Pb(IV), Te(IV), the transition metals Ni(II), Co(II), Cu(II), Fe(III), Cd(II), Hg(II), and the nonmetals I(I) and S(II).¹⁰ Ultrasound-assisted vapor generation has been proposed very recently for Hg(II)¹¹ and CH_3Hg^+ .¹²

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Table 1. Gas Chromatographic Conditions Employed in the GC-MS Identification and Determination of the Alkyl Derivatives

code	injector (°C)	transfer line (°C)	helium (mL min ⁻¹)	GC column	oven temperature program
GC-1 ^a	200	260	1.2	30 m, 100% PDMS (poly dimethyl siloxane) 0.25 mm i.d., 1 µm film thickness	35 °C for 5 min, 10 °C min ⁻¹ up to 180 °C, hold for 15 min.
GC-2 ^b	200	260	1.0	60 m, DB624 (94% poly dimethyl siloxane, 6% cyanopropylphenylsiloxane), 0.25 mm i.d., 1.4 µm film thickness	35 °C for 10 min, 10 °C min ⁻¹ up to 250 °C, hold for 5 min.

^a Varian 3400CX gas chromatograph. ^b TRACE2000 gas chromatograph, Thermo-Electron.

Table 2. Volatile Reaction Products Identified after the Hydrolysis of TMOT and TEOT in Water^a

TMOT			TEOT		
retention time (min)	reaction product	relative signal	retention time (min)	reaction product	relative signal
2.68	CH ₃ F	0.0076	2.94	CH ₃ CH ₂ F	0.056
3.26	(CH ₃) ₂ O	100	4.36	CH ₃ OCH ₂ CH ₃	0.2
4.29	CH ₃ OH	2.2	6.21	CH ₃ CH ₂ OH	1.7
4.37	CH ₃ OCH ₂ CH ₃	12	6.46	(CH ₃ CH ₂) ₂ O	100
6.19	CH ₃ CH ₂ OH	0.047			
6.46	(CH ₃ CH ₂) ₂ O	0.23			

^a GC-MS: TRACE2000 Thermo-Electron, GC Conditions: GC-2. See Table 1.

Meerwein and coworkers¹³ discovered in 1937 a new class of highly effective alkylating agents, trialkyloxonium salts, which find large application as alkylating agents in organic chemistry.¹⁴ This paper reports, for the first time, a study on the application of trialkyloxonium tetrafluoroborates R₃O⁺BF₄⁻ (R=Me, Et) to the aqueous phase derivatization of simple inorganic species into volatile and relatively stable alkylated species of defined chemical structure, with the final aim to perform their separation and determination in aqueous samples. In the present paper the attention is mainly devoted to establish the principle of the method, discussing mainly on fundamental aspects and analytical potentialities.

EXPERIMENTAL SECTION

Chemicals. Trimethyloxonium tetrafluoroborate (TMOT) (purity ≥ 98%) and triethyloxonium tetrafluoroborate (TEOT) (purity ≥ 97%) were obtained from Fluka. One M TEOT in CH₂Cl₂ (Fluka). More concentrated aqueous solution, about 2 M TEOT (about 400 mg in 1 mL H₂O) were prepared in order to counterbalance the amount of reagent which is lost by hydrolysis. The aqueous solution of TEOT must be added to the sample within 5 min from its preparation. Aqueous stock solution of the analytes (1000 µg mL⁻¹) were prepared from analytical grade reagents. More diluted solutions were prepared just before use. Pesticide grade CH₂Cl₂ (Carlo Erba) was employed for preparation of internal standard solutions. A 2.5 M NaBH₄ stock solution was prepared by dissolving the solid reagent (98%, Aldrich) in 1 M NaOH (30%, Trace Select, Fluka) and filtering on 0.45 µm membrane. The solution was stable for a week if stored refrigerated. More diluted solutions were prepared just before use. Ultrapure water prepared with a

purification system (Purelab Classic, USF) was employed in all the operations.

Apparatus. Gas chromatography mass spectrometry (GC-MS) was employed for both identification and determination of reaction products. A 3400CX gas chromatograph (Varian) equipped with a 1077 split-splitless injector was directly interfaced with a Saturn 3 ion trap mass spectrometer (Varian). For some experiments a Thermo-Electron GC-MS system was employed, which comprised a Trace 2000 Thermo-Electron GC equipped with a quadrupole mass filter DSQ Thermo-Electron. The GC columns and operating conditions are reported in Table 1.

Reactions were conducted in screw-capped reaction vials fitted with PTFE/silicone septa (Pierce Chemical Co.). Gas tight syringes of 0.5 mL and 5 µL volume (Scientific Glass Engineering) were employed for the injection of gas and liquid samples, respectively.

Determination of iodide by ion chromatography (IC) was performed by a Dionex DX500 apparatus composed by IP20 isocratic pump and ED40 electrochemical detector operating in integrated amperometric mode with silver working electrode. Separations were performed on AG7 medium-high capacity hydrophilic exchanger (50 mm × 4 mm i.d.), with 0.05 M HNO₃ as the eluent at 1.5 mL min⁻¹, and injecting 100 µL of aqueous sample.

Procedures. For the qualitative identification of gaseous reaction products, TMOT or TEOT 40 mg solid reagents were placed in a 4 mL vial. The vial was purged with argon before the addition of 100 µL of analyte aqueous solution (100–1000 µg mL⁻¹). The solution was left to react for 5 min in the case of TMOT and for 40 min in the case of TEOT. A headspace of 250 µL was injected in the GC-MS apparatus.

For the identification of the less volatile reaction products, 100 µL of TEOT/ CH₂Cl₂ reagent solution were placed in a 750 µL insert, which was fitted in a 4 mL reaction vial. After purging with argon 200 µL of 1000 µg mL⁻¹ analyte aqueous solution were injected and the solution left to react for 10 min, and 1 µL of organic layer injected into GC-MS.

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Table 3. Volatile Reaction Products Identified by Headspace Analysis after the Alkylation of Different Substrates with TMOT and TEOT

substrate	TMOT		TEOT		conditions (see Table 1)
	retention time (min)	products	retention time (min)	products	
Cl ⁻	3.43	CH ₃ Cl	3.62	CH ₃ CH ₂ Cl	GC-2
Br ⁻	2.02	CH ₃ Br	3.26	CH ₃ CH ₂ Br	GC-1
I ⁻	3.05	CH ₃ I	5.51	CH ₃ CH ₂ I	GC-1
CN ⁻	2.33	CH ₃ CN	3.80	CH ₃ CH ₂ CN	GC-1
SCN ⁻	7.94 9.13	CH ₃ SCN (100) ^a CH ₃ NCS (3) ^a	10.32 11.00	CH ₃ CH ₂ SCN (100) ^a CH ₃ CH ₂ NCS (7) ^a	GC-1
S ²⁻	3.07	(CH ₃) ₂ S	8.48	(CH ₃ CH ₂) ₂ S	GC-1
NO ₃ ⁻	10.75	CH ₃ O-NO ₂	14.95	CH ₃ CH ₂ O-NO ₂	GC-2
NO ₂ ⁻	3.83	CH ₃ O-NO	5.28	CH ₃ CH ₂ O-NO	GC-2

^a Relative signal intensity.

Chemical identity of reaction products generated after alkylation by TMOT or TEOT was confirmed by comparison of experimental mass spectra with the mass spectra stored in the NIST05 libraries of GC-MS instruments.

The analytical procedure was performed by using only the TEOT derivatization. For headspace analysis 2 mL of the aqueous sample were placed in 4 mL vial and sealed. After flushing the headspace with argon 5 μ L of CH₂Cl₂ internal standard solution (1% of CH₂Cl₂ in ethanol) were added and sonicated for 5 min. A 100 μ L aqueous solution of TEOT (about 2 M) was injected and the solution was left to react at room temperature for 3 h, and 250 μ L of headspace were injected into GC-MS apparatus. For liquid phase analysis a 300 μ L of aqueous sample solution was placed in a 750 μ L insert, which was fitted in a 4 mL vial, and 50 μ L of internal standard solution (0.15 g toluene in 100 g CH₂Cl₂). After sealing with a screw cap 300 μ L of 1 M TEOT in CH₂Cl₂ were injected and the vial was shaken and left to react at room temperature for 24 h. 1 μ L of organic extract was injected into GC-MS apparatus.

Determination of bromide in groundwater reference material (BCR-612) and iodine in table salt were performed by headspace analysis following TEOT derivatization, according to the procedure described above. The quantification was performed by the analyte addition method. For determination of bromide and iodide using headspace analysis, CH₂Cl₂ was found to be appropriate as an internal standard for EtBr and EtI determination. It has similar characteristic in terms of volatility, aqueous solubility and it is chemical stable in reaction medium, but different retention time. In addition it can be achieved with high degree of purity. In the case of liquid phase extraction, CH₂Cl₂ was replaced by toluene, which possesses also suitable characteristic of volatility, solubility, chemical inertness, and retention time.

Prereduction of Iodate to Iodide. A prereduction step of iodate to iodide was necessary for the analysis of table salt in which iodine is under form of iodate (see section on Prereduction of Iodate with NaBH₄). Prereduction was performed by adding 100 μ L of 0.25 M NaBH₄ in 1 M NaOH, to 2 mL of aqueous sample (2 mg mL⁻¹ of table salt) in a 4 mL reaction vial. The solution was allowed to react for 24 h in order to allow the hydrolysis of NaBH₄ and by leaving the vial not tightly capped in order to left the evolving hydrogen to flow out. Then the vial was tightly capped and analytical procedure above-described for TEOT derivatization was applied.

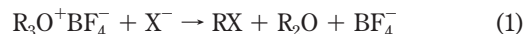
Safety Considerations. TMOT and TEOT are solid, non volatile reagents, but they are powerful alkylating agents and must be managed with caution.

The hydrolysis of TMOT and TEOT produce volatile, flammable organic reaction products such as dimethyl- and diethyl ether, methyl and ethyl alcohol. Hydrolysis of NaBH₄ produces hydrogen.

Reactions are conducted in sealed vials, placed under fume hood. Caution must be used due the pressure buildup following the hydrolysis of reagents. The excess of pressure must be removed before opening the vial at the end of experiments.

RESULTS AND DISCUSSION

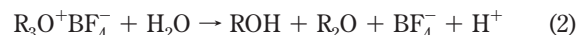
Aqueous Phase Reactions of Trialkyloxonium Tetrafluoroborates. The aqueous phase reaction of simple anionic species with trialkyloxonium tetrafluoroborates can be described by the reaction:



where R₃O⁺ acts as a source of R⁺ toward organic and inorganic nucleophilic species.¹⁴

The mechanism of reaction 1, leading to formation of alkylated nucleophile, RX, is reported to be largely controlled by the S_N1 ionization reaction step, Et₃O⁺ → Et⁺ + Et₂O, in the case of TEOT reaction with halogen anions, Cl⁻, Br⁻ and I⁻.¹⁵

Simultaneously, R₃O⁺ undergoes hydrolysis which is accompanied by the formation of an alcohol and an ether, and by a sharp decrease of pH due to the formation of protons:

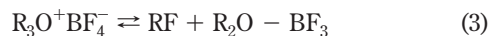


TEOT undergoes hydrolysis with a half-life 7.4 min at 25°, independently of acidity in the range of pH from 4 to 9, and complete decomposition in 80 min at 18 °C.¹⁴ TMOT undergoes faster hydrolysis being completely hydrolyzed in 8 min at 18 °C.¹⁴

The generation of RX species is therefore controlled by the competition between reactions 1 and 2. Reutov^{14,16} reported generation efficiencies of 12, 23, 53, 64, and 55% for aqueous phase

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and/or by the alkylation of fluoride generated by reaction hydrolysis of tetrafluoroborate¹⁷



The poor reaction efficiency of fluoride with R_3O^+ and reactions 3 and 4, makes the CVG by alkylation by R_3O^+ ($R=Me, Et$) unsuitable for fluoride determination.

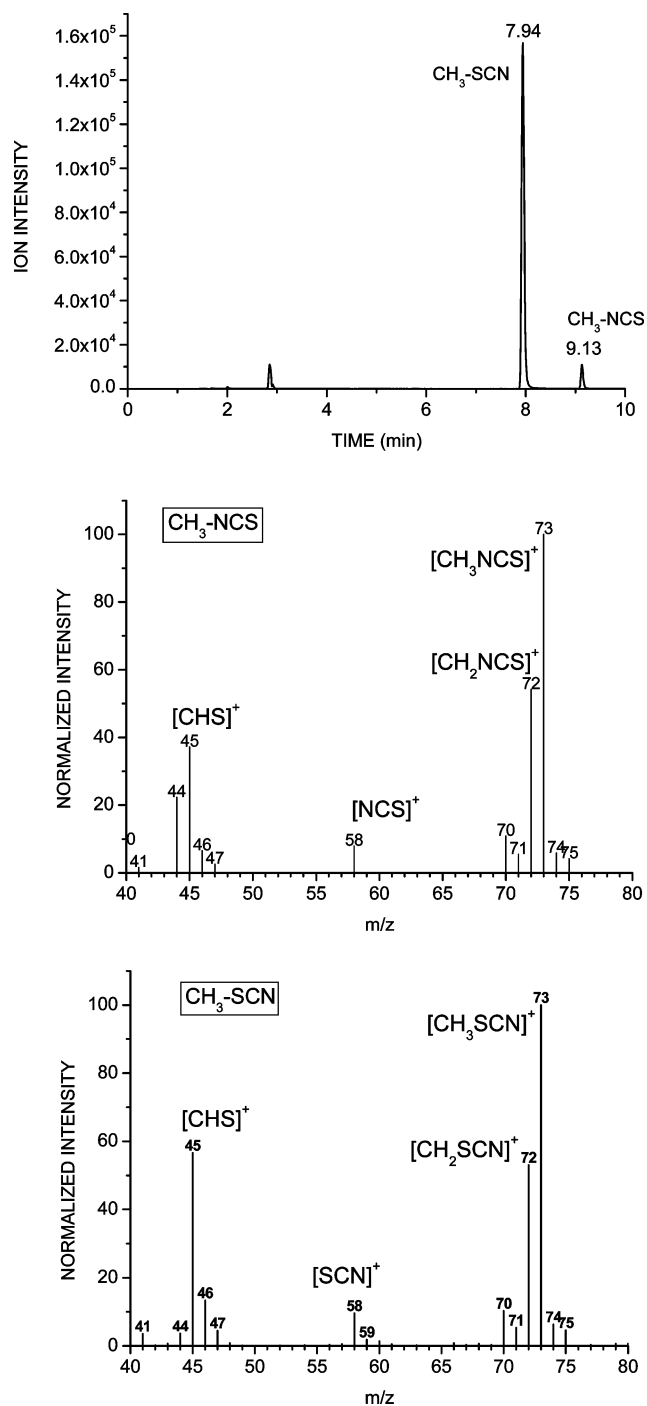


Figure 1. Separation and identification by GC-MS of reaction products obtained by aqueous phase methylation (40 mg TMOT) of thiocyanate (0.1 mL of 1000 $\mu\text{g mL}^{-1}$).

ethylation by TEOT of Cl^- , Br^- , I^- , SCN^- and CN^- , respectively, while ethyl fluoride was obtained with very poor efficiency (substrate concentrations and reagent to substrate ratio are not given).

GC-MS analysis of headspace volatile species generated by hydrolysis of TMOT and TEOT are reported in Table 2. For TEOT the hydrolysis products are those expected from reaction 2, while for TMOT some impurities of the ethylated reagent are evident. In both cases a significant amount fraction of alkylated fluorides has been detected, which is likely to be generated by the equilibrium reaction

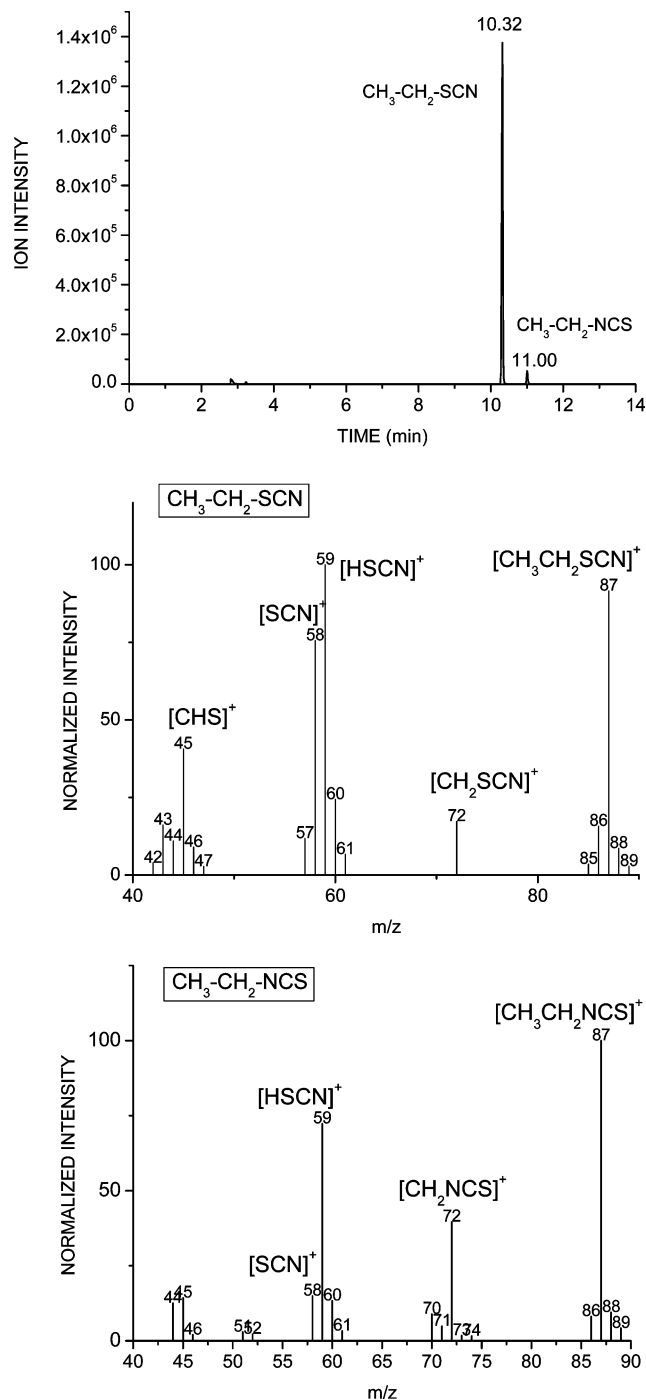


Figure 2. Separation and identification by GC-MS of reaction products obtained by aqueous phase ethylation (40 mg TEOT) of thiocyanate (0.1 mL of 1000 $\mu\text{g mL}^{-1}$).

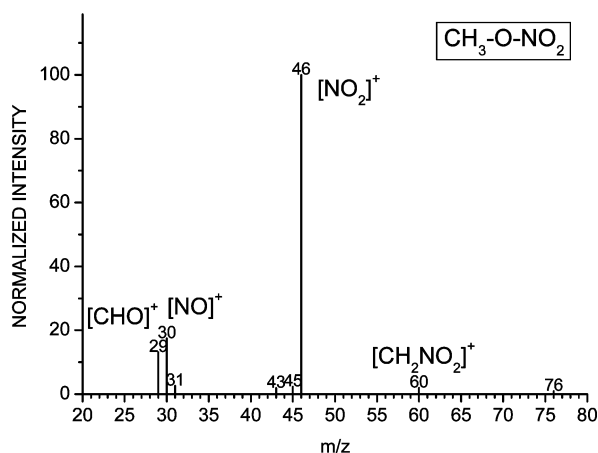
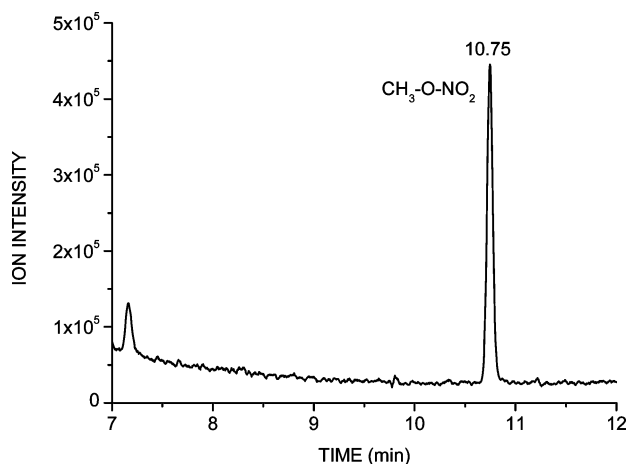


Figure 3. Separation and identification by GC-MS of reaction products obtained by aqueous phase methylation (40 mg TMOT) of nitrate (0.1 mL of 1000 $\mu\text{g mL}^{-1}$).

In general, both TMOT and TEOT are not easy to manipulate due to their hygroscopicity. They must be handled and stored in dry atmosphere in order to avoid decomposition by hydrolysis. Preparation of stock solutions is not easy due to the extreme reactivity of TMOT and TEOT with most of chemical functionalities. TEOT is soluble in CH_2Cl_2 , whereas TMOT is not soluble in this solvent. TEOT solution in CH_2Cl_2 are stable and commercially available. They can be used for derivatization-extraction procedures, but are not suitable for headspace analysis of aqueous solutions.

The reactivity of TMOT and TEOT make difficult also pH adjustment using buffers because they react with the chemical functionalities (for example, $-\text{OH}$, $-\text{COOH}$, NH_3 , NH_2R , NHR_2 , RNR_3 , etc) which are typically present in buffer solutions. For these reason all reactions were performed in pure aqueous media. The only exception is NaOH, the effect of which has been investigated in the determination of iodate as reported in the relevant section.

Reaction Products. The aqueous phase alkylation with TMOT and TEOT was tested on a number of different inorganic substrates such as, Cl^- , Br^- , BrO_3^- , I^- , IO_3^- , SCN^- , SeCN^- , CN^- , S^{2-} , NO_3^- , NO_2^- , SO_3^{2-} , SO_4^{2-} , PO_4^- , boric acid, inorganic As(III), inorganic As(V), monomethylarsonic(V) acid, and dimethylarsinic(V). Reactions of the substrates to give the corresponding alkylated derivatives were successful only for

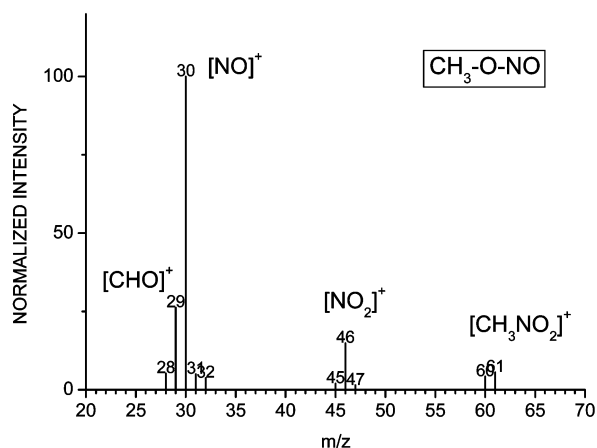
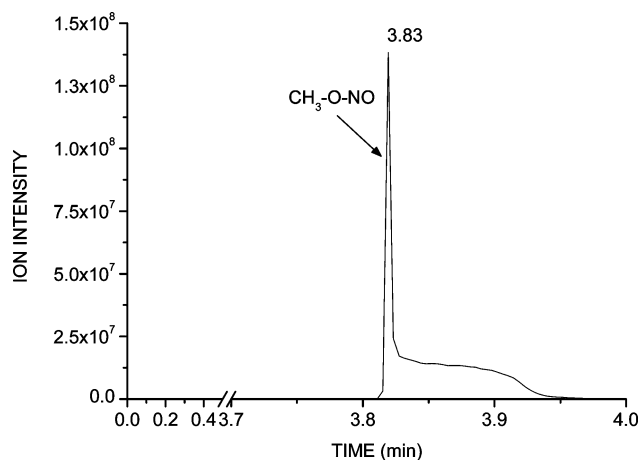


Figure 4. Separation and identification by GC-MS of reaction products obtained by aqueous phase methylation (40 mg TMOT) of nitrite (0.1 mL of 1000 $\mu\text{g mL}^{-1}$).

Cl^- , Br^- , I^- , SCN^- , CN^- , S^{2-} , NO_3^- , and NO_2^- for headspace analysis. (Table 3). Examples of GC-MS identification of some of the reaction products are reported in Figures 1–6. All the oxoanions failed to give volatile detectable species, with the only exceptions of nitrites and nitrates, which gave the alkyl esters arising from O-alkylation of the substrates (Figures 3–6). For the other oxoanions it is likely that O-alkylation takes place in many cases but the alkylated derivatives are unstable in aqueous solution and they hydrolyze to give the original substrates or they decompose during GC separation. For example, the alkyl esters of sulfuric and sulfurous acids,¹⁸ arsenic¹⁹ and arsenious²⁰ acids are reported to hydrolyze quite fast in aqueous solutions. Sulfur containing substrates give S-alkylation. In the case of thiocyanate, where both S-alkylation and N-alkylation are possible, the main product is the alkylthiocyanate $\text{R}-\text{S}-\text{C}\equiv\text{N}$. Only a small fraction of the substrate (<7%) undergoes N-alkylation to give the alkylisothiocyanate, $\text{R}-\text{N}=\text{C}=\text{S}$, with both TMOT and TEOT reagents (Figures 1 and 2). However, the homologous of thiocyanate, selenocyanate, reacts vigorously with both TMOT and TEOT. A fast increase of the pressure in the reaction vial was observed soon after the addition of alkylating agent and, almost simulta-

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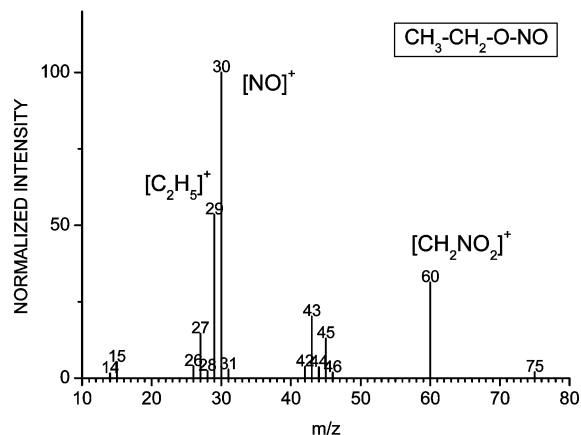
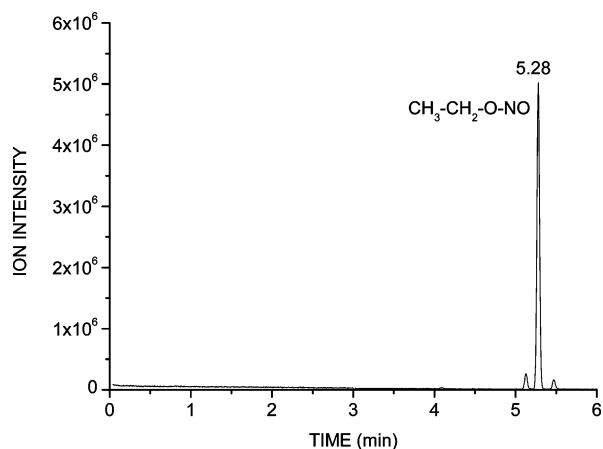


Figure 5. Separation and identification by GC-MS of reaction products obtained by aqueous phase ethylation (40 mg TEOT) of nitrite (0.1 mL of 1000 $\mu\text{g mL}^{-1}$).

neously, a red suspension, probably $\text{Se}(0)$, was observed in solution. No detectable products, other than hydrolysis products of TMOT and TEOT, were found in the headspace of reaction vessel, even lowering the concentration of selenocyanate down to 10 $\mu\text{g mL}^{-1}$.

The other possibility for which derivatization products cannot be detected in the headspace of reaction vial is that they present a limited volatility and/or they present a high affinity for the aqueous phase. A series of experiments was repeated by using a solution of TEOT in CH_2Cl_2 , which was placed in contact with the aqueous sample containing the substrate. In this case the reaction takes place at the liquid interface and the reaction products can be extracted in the organic phase. The GC-MS analysis of organic phase are reported in Table 4, and only the ethyl derivatives of I^- , SCN^- and S^{2-} could be detected. The experiments were not performed for those substrates, Cl^- , Br^- , CN^- , NO_3^- , NO_2^- , whose ethyl derivatives cannot be sufficiently separated from the peaks CH_2Cl_2 solvent peak.

Analytical Figures of Merits. Limits of detection (LOD) and upper limit of linear dynamic ranges (LDR) were investigated for TEOT derivatization. The results are reported in Table 5. Interesting LODs can be also achieved for iodide and thiocyanate using TEOT in CH_2Cl_2 and injecting the organic phase. Relatively poor LODs are obtained in headspace analysis for cyanide and thiocyanate in comparison with those of iodide and bromide in spite that the conversion efficiency of iodide, bromide, cyanide, and thiocyanate should be comparable.¹⁶ Blanks were

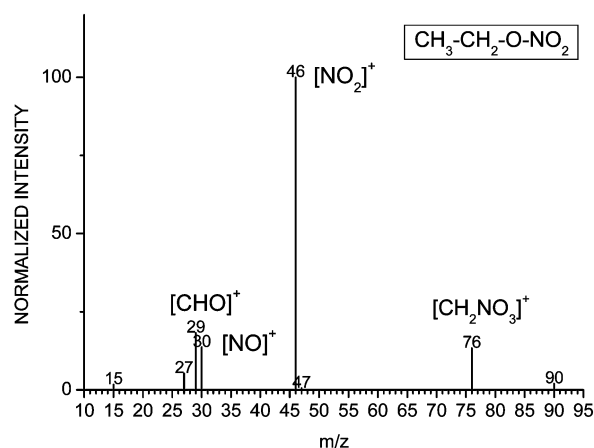
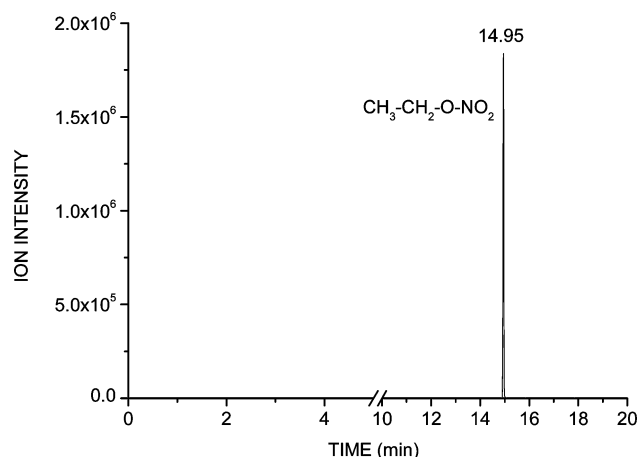


Figure 6. Separation and identification by GC-MS of reaction products obtained by aqueous phase ethylation (40 mg TEOT) of nitrate (0.1 mL of 1000 $\mu\text{g mL}^{-1}$).

Table 4. Reaction Products Identified in CH_2Cl_2 Organic Phase after the Alkylation of Different Substrates with TEOT

substrate	retention time (min)	products	conditions (see Table 1)
I^-	17.46	$\text{CH}_3\text{CH}_2\text{I}$	GC-2
SCN^-	26.56 27.29	$\text{CH}_3\text{CH}_2\text{SCN}$ (100) ^a $\text{CH}_3\text{CH}_2\text{NCS}$ (2) ^a	GC-2
S^{2-}	6.53	$(\text{CH}_3\text{CH}_2)_2\text{S}$	GC-2

^a Relative signal intensity.

not detectable for analytes reported in Table 5, and therefore reagents impurities did not contribute in any case to degradation of LODs. The lower volatility of EtSCN (bp 138 °C) with respect to EtI (bp 72 °C) and EtBr (bp 38 °C) is probably the reason for the higher LOD of thiocyanate. This is also confirmed by the evidence that comparable, higher LODs are obtained for iodide and thiocyanate by the TEOT/ CH_2Cl_2 procedure (see Table 5). For cyanide the higher LODs cannot be completely addressed to the lower volatility of EtCN (bp 97 °C). In this case, also its high hydrophilicity and solubility in water play a role, as it is confirmed by the evidence that no detectable EtCN is found in the organic phase using the TEOT/ CH_2Cl_2 procedure. In the case of sulfide the worst LOD could be addressed to the further alkylation of Et_2S to Et_3S^+ , which is non volatile in headspace procedure,

Table 5. Analytical Figures of Merit for the Determination of Some Species by Ethylation with TEOT and GC-MS

analyte	headspace analysis					liquid phase analysis				
	LOD ^a	upper limit ^b	R ²	GC-MS conditions		LOD	upper limit	R ²	GC-MS conditions	
	($\mu\text{g mL}^{-1}$)	($\mu\text{g mL}^{-1}$)		GC ^c	m/z^d	($\mu\text{g mL}^{-1}$)	($\mu\text{g mL}^{-1}$)		GC ^c	m/z^d
Cl [−]	0.028	100	0.9996 (0.1–100) ^e	GC-2	64 + 66	0.006	10	0.9999 (0.05–10)	GC-2	156
Br [−]	0.0026	10	0.9972 (0.01–10)	GC-1	108 + 110					
I [−]	0.0012	0.5	0.9999 (0.005–0.5)	GC-1	156					
CN [−]	0.28	2000	0.9999 (2–2000)	CG-1	54	0.01	100	1.000 (0.1–100)	GC-2	59 + 87
SCN [−]	0.28	960	0.9996 (1–100)	CG-1	59 + 87					
S ^{2−}	0.37	100	1.000 (1–100)	CG-1	75 + 90					
NO ₃ [−]	0.036	100	0.9999 (1–100)	GC-2	46					
NO ₂ [−]	0.20			GC-2	60					

^a Three times SD of baseline noise. ^b Upper limit of linear calibration graphs. ^c See Table 11 for GC conditions. ^d Extracted mass for quantification. ^e Concentration range ($\mu\text{g mL}^{-1}$) employed for estimation of R².

whereas it is almost completely partitioned in the aqueous phase in the TEOT/CH₂Cl₂ procedure.

Prereduction of Iodate with NaBH₄. NaBH₄ appears to be a convenient reductant for iodate to iodide because the final decomposition product, besides hydrogen, is H₃BO₃ which does not give any detectable product after reaction with TEOT. Reaction of TEOT with BH₄⁻ gives ethane,¹⁴ and reaction with OH⁻ gives ethanol (reaction 2). Thus, the concentration of both OH⁻ and BH₄⁻ should be kept much lower than TEOT (about 0.12 mol L⁻¹ in the sample solution) in order to avoid reagent consumption.

Optimization of the prereduction conditions of IO₃⁻ to I⁻ by BH₄⁻ was performed on pure solution of iodate. The acidity of iodate solution, measured before addition of BH₄⁻ solution, was varied from pH 5.6, the acidity of water in equilibrium with atmospheric CO₂, up to pH 14 by addition of NaOH. The amount of BH₄⁻, contained in 100 μL of 1 M NaOH solution, which were added to 2 mL of iodate solution was varied in the range of 2.5×10^{-7} – 2.5×10^{-5} moles. This corresponds to a concentration range of about 1.2×10^{-4} – 1.2×10^{-2} mol L⁻¹ of BH₄⁻ in the iodate solution. The reaction time was left to 24 h, which is necessary in order to allow most of the BH₄⁻ to hydrolyze. This was necessary to allow the hydrogen gas to left the reaction vial and to avoid the production of ethane following the reaction of TEOT with BH₄⁻. Overpressure in the vial made impossible a reliable and reproducible sampling of headspace gases for GC-MS analysis. The neutralization of alkalinity by addition of acids was not taken into consideration in order to avoid the introduction of anionic species. The results of optimization studies are reported in Figure 7. Following these results the prereduction was performed on pure aqueous sample, pH about 5.6, by adding 100 μL of 0.25 M BH₄⁻ in 1 M NaOH, to 2 mL of aqueous sample.

Applications to Real Samples. Considering that TMOT and TEOT present an elevated degree of reactivity with many inorganic and organic analytical substrates their application was tested on water samples, which do not require a preliminary chemical manipulation minimizing thus the introduction of unwanted chemical functionalities. The method based on TEOT alkylation and headspace analysis by GC-MS of ethylated derivatives was applied to the determination of both bromide and iodide.

Bromide was determined in BCR-612 groundwater certified reference material (Institute for Reference Materials and Measure-

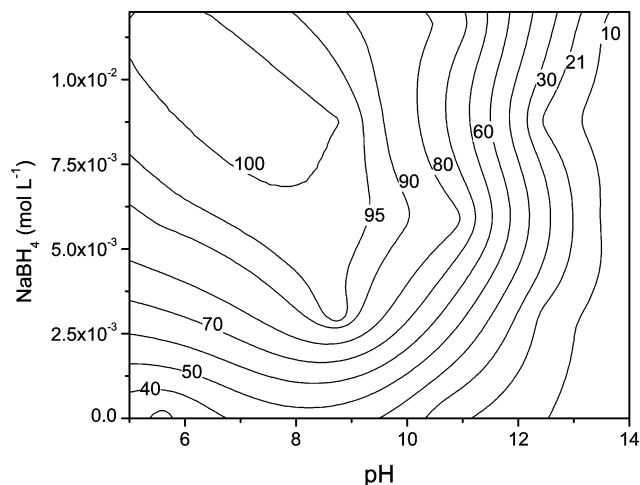


Figure 7. Effect of pH of aqueous solution (2 mL) containing iodate ($1 \mu\text{g mL}^{-1}$) and concentration of added NaBH₄ (0.1 mL in 1 M NaOH) on the recovery of iodate by aqueous phase ethylation and GC-MS determination (see experimental section for details on the procedure).

ments, Geel, Belgium). Groundwater was analyzed without any further manipulation, according to the procedure reported in the Experimental section. The result of $253 \pm 24 \mu\text{g kg}^{-1}$ of bromide (mean \pm standard deviation, $N = 5$) was in excellent agreement with the certified value of $252 \pm 10 \mu\text{g kg}^{-1}$ of bromide (uncertainty is the half width of the 95% confidence interval).

Determination of iodide was performed in a commercially available table salt after dissolution in water (2 mg mL^{-1}) and by using TEOT alkylation and headspace analysis GC-MS. Parallel analysis by ion chromatography was employed for comparison. Direct determination on dissolved sample gave no detectable signals with both TEOT/GC-MS and ion chromatography, indicating that iodide is present below detection limit and all iodine is present as iodate. Considering that iodate does not give any species which is detectable by GC-MS after derivatization with TEOT a prereduction step of iodate to iodide is necessary. After reduction of iodate to iodide with NaBH₄ the determinations performed by TEOT/GC-MS and IC gave $70 \pm 6 \mu\text{g g}^{-1}$ of I and $67 \pm 4 \mu\text{g g}^{-1}$ of I ($N = 5$), respectively, indicating a good agreement between the two methods. The recovery of iodate by TEOT/GC-MS method, was estimated by comparison of the calibration graph obtained by adding iodate to table salt solution (0, 0.025, 0.05, and $0.1 \mu\text{g mL}^{-1}$

iodate as I), with that obtained by iodide in pure solution. The slope of calibration graphs of added iodate to table salt solution and iodide in pure solution were $1.11 \pm 0.02 \text{ mL } \mu\text{g}^{-1}$ ($R^2 = 0.9996$) and $1.18 \pm 0.01 \text{ mL } \mu\text{g}^{-1}$ ($R^2 = 0.9998$), respectively, corresponding to a recovery better than 94% of iodate in table salt solution.

CONCLUSIONS

Trialkyloxonium "Meerwein" reagents have proven to perform aqueous phase alkylation of several inorganic substrates such as I^- , Br^- , Cl^- , S^{2-} , CN^- , SCN^- , NO_2^- , and NO_3^- , giving the possibility to separate them from reaction matrix under the form of volatile reaction products of defined chemical composition. The alkylated derivatives obtained, RI, RBr, RCl, RCN, RSCN, R_2S , RONO, and RONO_2 ($\text{R}=\text{Me}$, Et), present suitable stability to be determined by GC-MS at ultra trace level. The

disadvantage of trialkyloxonium reagents is that they are not easy to manipulate, undergoing a relatively fast hydrolysis. In perspective, the CVG based on alkylation by R_3O^+ , possessing most of the favorable features and potentialities of CVG methods—separation, preconcentration and selectivity—is open to significative improvements, to be achieved also through an optimization of reaction conditions (temperature, volume of the vial and of the sample, dynamic head space analysis, etc). It could find application in the determination and speciation of inorganic species or other species containing specific chemical functionalities.

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