# Trace Determination of Glycols by HPLC with UV and Electrospray Ionization Mass Spectrometric Detections

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**A high-performance liquid chromatography/mass spectrometry (HPLC/MS) method is developed for trace determination of glycols (ethylene glycol, 1,2- and 1,3-propylene glycols, and 2,3-butylene glycol) in water after derivatization with benzoyl chloride. Benzoyl esters of glycols are separated by microcolumn reversed-phase HPLC. Sensitivity and linearity of UV detection at 237 nm is compared with electrospray ionization mass spectrometric (ESI-MS) detection using selected ion monitoring. Limits of detection (LOD) and quantitation (LOQ) for UV detection are 1 and 2 mg/L, respectively. For ESI-MS detection, LOD and LOQ are in the ranges 10−25 and 20−50 μg/L, respectively. LOD obtained by ESI-MS for the determination of glycols is improved by 2−3 orders of magnitude in comparison to previously published methods. The effect of the structure of isomeric glycols on their electrospray mass spectra is discussed. The method has been applied for the determination of glycols in aqueous matrixes containing high concentrations of salts occurring in nuclear waste disposal treatment.**

Ethylene glycol (EG) and other glycols—1,2-propylene glycol (1,2-PG), 1,3-propylene glycol (1,3-PG), and 2,3-butylene glycol (2,3-BG)—are widely used as components of antifreeze liquids and of other commercial products.[1] EG is toxic for humans; the toxicity of other glycols is lower.[2−4] Furthermore, glycols as well as other complexing organic molecules (such as carboxylic acids, ketones, or aldehydes) are present in the leaching products of bitumen which are used as nuclear waste matrixes. The wastes contain 60% bitumen (in weight) and 40% salts ($NaNO_3$ mainly, $Na_2SO_4$ and others) coming from the reprocessing process as well as several radionuclides. Therefore, in the framework of nuclear waste disposal studies, it is important to investigate the complexing properties of these compounds since they could affect radionuclide mobility. For that purpose, a very sensitive and selective technique is required for the determination and quantification of these organic compounds, especially glycols, in these very salty leachates.

Enzymatic,[5−7] fluorimetric,[8] or colorimetric[9,10] methods for the determination of EG after its oxidation to formaldehyde are nonspecific. GC assay is more specific, but problems with peak tailing and carryover effects are observed.[11−14] Limits of detection and quantitation of 0.5 and 2 mg/L are reported for the GC determination of EG[15] and also for the GC assay of glycols after phenyl boronate derivatization.[16] The derivatization with *n*-hexyl chloroformate followed by GC/MS can be applied for a wide range of hydrophilic (poly)hydroxy compounds,[17] but the derivatization of glycols is incomplete because of their lower reactivity, as was confirmed by our preliminary experiments.

Trace determination of hydrophilic compounds in aqueous matrixes is more difficult than the analyses of hydrophobic compounds. Typical preconcentration steps useful for hydrophobic compounds as solid-phase extraction or liquid−liquid extraction from water to a nonpolar solvent usually fail because of too low recoveries. One of the most sensitive detection methods for HPLC is mass spectrometry with atmospheric pressure ionization (API), which also offers valuable structural information. The sensitivity of API is reduced for compounds with lower molecular weights because of increased noise due to the occurrence of various molecular adducts attributed to the mobile phase. Hence, sensitive API-MS detection of EG, PG, and BG without the derivatization would be difficult, because their molecular masses are 62, 76, and 90 Da, respectively.

Last but not least, benzoyl substituents of low polarity considerably enhance the selectivity of separation of the derivatives of individual glycols with respect to the separation of underivatized compounds, which makes possible unambiguous assessment of

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Table 1. Percent Relative Intensity and *m/z* Values (in Parentheses) of the Most Abundant Ions in Electrospray Mass Spectra of Dibenzoyl Derivatives of Various Diols and of Phenol as the Internal Standard[a]

| compd | ring ion[b] | $[M + H - C_6H_5COOH]^+$ | $[M + H]^+$ | $[M + Na]^+$ | $[M + K]^+$ | $[M + Na + ACN^c]^+$ |
|---|---|---|---|---|---|---|
| EG | 5 | 100 (149) | 4 (271) | 21 (293) | 1.1 (309) | 16 (334) |
| 1,3-PG | 6 | 100 (163) | 4 (285) | 11 (307) | 0.6 (323) | 8 (348) |
| 1,2-PG | 5 | 100 (163) | 5 (285) | 30 (307) | 1.9 (323) | 23 (348) |
| 1,3-BG | 6 | 100 (177) | 5 (299) | 13 (321) | 0.6 (337) | 9 (362) |
| 2,3-BG | 5 | 100 (177) | 5 (299) | 47 (321) | 2.1 (337) | 28 (362) |
| 1,4-BG | 7 | 100 (177) | 17 (299) | 26 (321) | 0.9 (337) | 13 (362) |
| DEG[d] | 5 | 100 (193) | 4 (315) | 64 (337) | 0.8 (353) | 9 (378) |
| phenol | | | 199 | 221 | 237 | 262 |

[a] $[M + H - C_6H_5COOH]^+$ ions are the base peaks in all mass spectra. [b] Number of atoms in the ring structure of the $[M + H - C_6H_5COOH]^+$ ion. [c] Acetonitrile. [d] DEG means the derivative of diethylene glycol.

chromatographic peaks. Underivatized glycols are very polar and would be only weakly retained so that their separation from high concentrations of the inorganic salts in reversed-phase systems would be much more difficult than with their dibenzoyl esters. The salts would interfere not only with ESI-MS detection but also with the UV detection.

HPLC assay with UV detection after derivatization with benzoyl chloride was described for the determination of EG[18] or both EG and 1,2-PG with LOD and LOQ 10 and 20 mg/L, respectively.[19] Our present method offers a 10-fold improvement of the LOD of UV detection in comparison to previous work. The ESI-MS detection in the selected ion monitoring mode is nearly 2 orders of magnitudes more sensitive than the UV detection, and the occurrence of interfering peaks or the possibility of peak misidentification is significantly reduced.

The derivatization of glycols with benzoyl chloride solves all major problems mentioned above: (1) decreased polarity of the derivatives facilitates the solid- or liquid-phase extraction preconcentration step; (2) derivatization of diol groups improves the chromatographic behavior of the derivatives with respect to the nonderivatized glycols; (3) incorporation of two strong chromophores makes possible sensitive HPLC determination with UV detection; (4) increase in the molecular masses of derivatives by 208 Da improves the signal-to-noise ratio with ESI-MS detection because the intensity of the background noise is significantly reduced at higher masses.

## EXPERIMENTAL SECTION

**Chemicals.** Ethylene glycol, 1,2-propylene glycol, 1,3-propylene glycol, 2,3-butylene glycol, 1,3-butylene glycol, and 1,4-butylene glycol were purchased from Fluka (Buchs, Switzerland), acetonitrile, HPLC grade, was obtained from Merck (Darmstadt, Germany), and pentane, benzoyl chloride, phenol, benzyl alcohol, uracil, 30% sodium hydroxide, and potassium chloride were purchased from Sigma-Aldrich (Steinheim, Germany).

**HPLC Apparatus and Conditions.** The derivatives were separated in a reversed-phase HPLC system on a Capcell Pack C18 column (150 × 1 mm i.d., 5 $\mu$m particle size) obtained from Shiseido (Paris, France). The mobile phase, 55% acetonitrile in water, was premixed and continuously degassed by a Degasys DG-1210 vacuum degasser (Uniflows, Tokyo). A flow rate of 50 $\mu$L/min, an injection volume of 1 $\mu$L, and ambient temperature were used in all analyses.

For the analysis with UV detection, a PU-980 liquid chromatograph (Jasco, Tokyo) equipped with a Kontron 432 UV detector (Kontron Instruments, Milan, Italy) was employed. For analysis with ESI-MS detection, an HP 1100 liquid chromatograph (Hewlett-Packard, Palo Alto, CA) was used.

**MS Apparatus and Conditions.** Electrospray ionization mass spectrometric detection of positive ions was performed on a Quattro II mass spectrometer (Micromass, Manchester, England). Selected ion monitoring (SIM) of ions with $m/z$ = 199, 293, 307, 321, 334, 348, and 362 (see Table 1) was used for the HPLC/MS analysis (dwell 0.1 s, span 1 Da, interchannel delay 0.01 s). These seven ions for SIM were selected on the basis of the mass spectra of the individual compounds measured in the full scan mode from $m/z$ = 100 to 400. The cone voltage was set to 40 V, the source temperature was set to 70 °C, and a voltage of 3.50 kV was applied on the capillary outlet.

**Standard Solutions.** A standard stock solution containing 500 mg/L of each glycol (EG, 1,2-PG, 1,3-PG, 2,3-BG) in water was prepared. The working standard solution was obtained by diluting 100 times. Benzoyl alcohol at a concentration of 200 mg/L was used as the internal standard for the UV detection; phenol at a concentration of 500 mg/L was used for the electrospray detection. All standard solutions were kept at 5 °C and were stable for at least 1 month. The working standard solution of glycols was diluted appropriately with water to prepare the calibration standards in the concentrations 1, 2.5, 5, 10, 20, and 50 mg/L for the UV detection and 20, 50, 100, 250, and 1000 $\mu$g/L for the ESI-MS detection.

**Derivatization Procedure.** The Schotten−Baumann method of the benzoylation of glycols[19] in aqueous solution using an excess

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of the derivatization agent in a strongly alkaline medium was employed for the derivatization of EG, 1,2-PG, 1,3-PG, and 2,3-BG. The reaction follows the general reaction scheme $R(OH)_2 + 2C_6H_5COCl + 2NaOH \rightarrow R(OCOC_6H_5)_2 + 2NaCl$.

A mixture of 1 mL of working standard solution of glycols or of a real sample with addition of the internal standard solution (30 $\mu$L of benzyl alcohol standard for the UV detection or 100 $\mu$L of phenol standard for the ESI-MS detection), of 700 $\mu$L of 30% NaOH, and of 20 $\mu$L of benzoyl chloride was shaken for 10 min using a Top-Mix 94323 mixer (Bioblock Scientific, Heidolph, Germany). Then, 1 mL of pentane was added to the reaction mixture, the mixture was shaken, and 0.7 mL of the pentane phase was collected. Again, 1 mL of pentane was added to the aqueous phase, and after thorough mixing, 1 mL of the pentane phase was collected. Special care was taken not to collect any trace of aqueous phase. A total volume of the collected pentane extracts (1.7 mL) was evaporated at ambient temperature under a small stream of nitrogen. The residue was redissolved in 100 $\mu$L of 55% acetonitrile−water for the UV detection (or in 50 $\mu$L for the ESI-MS detection), and 1 $\mu$L was injected into the liquid chromatograph. The calibration curves were plotted as the ratios of the peak areas of each glycol to the peak area of the internal standard.

## RESULTS AND DISCUSSION

**Derivatization Procedure.** As was discussed in the introduction, the main objective of the present work to develop a sensitive and selective method for the determination of trace concentrations of glycols in matrixes containing high concentrations of inorganic salts. Principally, it would be possible to separate the glycol derivatives by HPLC directly in the reaction mixture after derivatization, as the salts would be eluted close to the column dead volume and would not interfere with the determination of glycols. However, the excess of the benzoyl chloride reagent and the reaction byproducts (benzoic acid and benzoic acid anhydride) would be retained more strongly and may interfere with the determination, as their concentrations in the reaction mixture could be several orders of magnitude higher than the concentrations of the dibenzoyl glycols. Hence, the reaction mixture was extracted with pentane to separate the derivatives of the glycols from the reaction mixture before their HPLC separation. The extraction procedure used led to 20-fold sample enrichment for the method with ESI-MS detection or 10-fold enrichment for the method with UV detection.

The recovery of the extraction procedure was tested using the pure EG derivative prepared by the preparative derivatization and recrystallization from pentane. The purity was checked by HPLC. Approximately 0.2 mg of pure EG derivative was added to 3 mL of pentane and 3 mL of water, and the mixture was agitated for 5 min. Then the aqueous and the organic phases were separated, and both phases were analyzed after suitable dilution by HPLC. The distribution coefficient of the EG derivative between pentane and water determined in this way was higher than 500. This means that using a two-stage extraction (see Experimental Section, Derivatization Procedure), less than 0.16% EG derivative is lost during the extraction procedure, which can be neglected.

The recovery of the whole derivatization procedure, including pentane extraction and evaporation, was tested by comparing the peak area of the derivative produced from a known amount of EG with the peak area of the pure EG derivative under identical HPLC conditions (see Experimental Section). The recovery of approximately 40% was reproducible under the conditions used for samples with different concentrations of EG. This means that derivatization is not complete under the conditions used. No peaks with the mass spectra corresponding to the monoester glycol derivatives were found in the chromatograms of the extracts after the derivatization procedure, which means that the monobenzoyl glycols either are not formed during the derivatization procedure or are completely separated from the dibenzoyl derivatives by extraction with pentane. On the other hand, a small peak with a mass spectrum corresponding to benzoic acid anhydride was found in the chromatogram. The area of this peak increased with decreasing concentration of glycols in the reaction mixture. This peak is separated from the later eluted peaks of dibenzoyl glycols and does not interfere with the determination.

The yields of the derivatization procedure with the standard solutions of glycols in pure water and in aqueous salt solutions containing 10 and 100 g/L KCl were compared, and no influence of the salt on the recovery of the method was observed, at least up to 100 g/L KCl.

**Internal Standards.** The incomplete recovery of the derivatization reaction makes necessary the addition of a suitable internal standard to the sample before the derivatization procedure for a reliable quantitation. Benzyl alcohol was selected as the internal standard for the UV detection, but it cannot be used with the ESI-MS detection because of low response. Phenol was found suitable as the internal standard for the ESI-MS detection in the SIM mode, despite coelution of phenol and EG derivatives. The monitoring of selected ions attributed unambiguously to phenol and to the EG derivatives makes possible the quantitation without their chromatographic separation. We selected the ions $[M + Na]^+$ ($m/z$ = 293−321) and $[M + Na + \text{acetonitrile}]^+$ ($m/z$ = 334−362) for the glycol derivatives and the protonated molecular ion ($m/z$ = 199) for the phenol derivative (see Table 1).

**Detection Conditions.** As the benzoyl moieties strongly absorb in the UV region, UV detection is suitable for the determination of dibenzoyl derivatives. For the best sensitivity, we selected the wavelength of the absorption maximum at 237 nm for detection.

To select best detection conditions for the positive-ion electrospray ionization, mass spectra of the derivatives of EG, 1,2- and 1,3-PG, 1,2-, 1,3-, 1,4-, and 2,3-BG, phenol, diethylene glycol, and other poly(ethylene glycol)s were recorded in the full scan mode from $m/z$ = 100 to 400. The spectra contain characteristic adducts of the molecular ions, i.e., $[M + H]^+$, $[M + Na]^+$, $[M + K]^+$, and $[M + Na + ACN]^+$. The relative abundances and masses of important ions are listed in Table 1. However, the most abundant ions in the mass spectra of all dibenzoyl glycol derivatives are the fragment ions $[M + H - C_6H_5COOH]^+$, formed by the loss of benzoic acid from the protonated molecular ions. We suggest a stable ring structure for these ions (Figure 1), which could explain the high relative intensity of these ions in the spectra of all studied glycols. The ring structures are more stable for a six-member ring (1,3-diols) than for a five- (1,2-diols) or a seven-member ring (1,4-diols), as suggested by the ratios of the intensities of $[M + Na]^+$ ions related to the intensities of the $[M + H - C_6H_5COOH]^+$ ions (Table 1)—11−13% for derivatives of 1,3-PG or 1,3-BG with the six-member ring, 21% for EG, 30% for

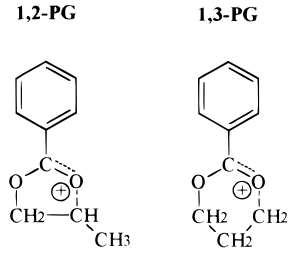


Figure 1. Suggested ring structures of the ions $[M + H - C_6H_5COOH]^+$ for the 1,2-propylene glycol derivative (a five-member ring) and the 1,3-propylene glycol derivative (a six-member ring).

1,2-PG, and 47% for 2,3-BG with the five-member ring ions, and 26% for the seven-member ring of 1,4-BG. The same trends are observed for the relative intensities of the $[M + K]^+$ and the $[M + Na + acetonitrile]^+$ ions. Even though the base peaks of cyclic ions yield the highest MS response, the ion of EG with $m/z = 149$ would not be suitable for practical analysis because the ion with the same mass is present in the mass spectra of phthalates, very frequent contaminants in various environmental samples. To avoid possible interferences caused by phthalates, the intense ions $[M + Na]^+$ and $[M + Na + ACN]^+$ were selected for monitoring of all glycols at the highest signal-to-noise ratio. The ion $[M + H]^+$ ($m/z = 199$), which is the base peak in the electrospray spectrum of phenol, was selected for the monitoring of the internal standard. The mass spectrometer was tuned to maximize the signal-to-noise ratio for these ions.

**HPLC Conditions.** The derivatives of EG, 1,2-PG, 1,3-PG, and 2,3-BG were separated by reversed-phase HPLC with 55% acetonitrile−water as the mobile phase. The selection of chromatographic conditions was dictated by the requirement of maximum sensitivity of determination.

The extraction procedure followed by evaporation of pentane used as the extraction solvent yields a limited volume of the final sample. Hence, a microcolumn with a 1 mm i.d. was preferred to larger diameter conventional analytical columns because of a lower peak dispersion and higher concentration of separated compounds at the column outlet. A sample injection volume of 1 $\mu$L was selected to use full column capacity for maximum sensitivity (higher injection volumes cause a decrease in the chromatographic resolution). Common flow rates with a 1 mm i.d. microcolumn are in the range of tens of $\mu$L/min, which makes it possible to introduce the effluent from the column directly to the electrospray ion source without using a postcolumn effluent split as with large-diameter columns. The effluent split would lead to a less efficient use of the limited sample volume and also to a lower reproducibility of quantitation. A flow rate of 50 $\mu$L/min was used throughout this work.

The chromatographic system with a microcolumn needs extracolumn volumes as low as possible to avoid excessive peak broadening and/or tailing. The dead volume of the whole chromatographic system including the microcolumn was measured as the elution time of uracil and was 72 $\mu$L. Careful washing of the sample loop and of the injection syringe after each injection suppresses sample carryover effects.

**Evaluation and Comparison of the Determinations Using UV and ESI-MS Detection.** Figure 2 shows the chromatogram of the derivatives of EG, 1,2-PG, 1,3-PG, and 2,3-BG and benzyl alcohol as the internal standard (concentration 10 mg/L each) using UV detection at the absorption maximum of 237 nm. The

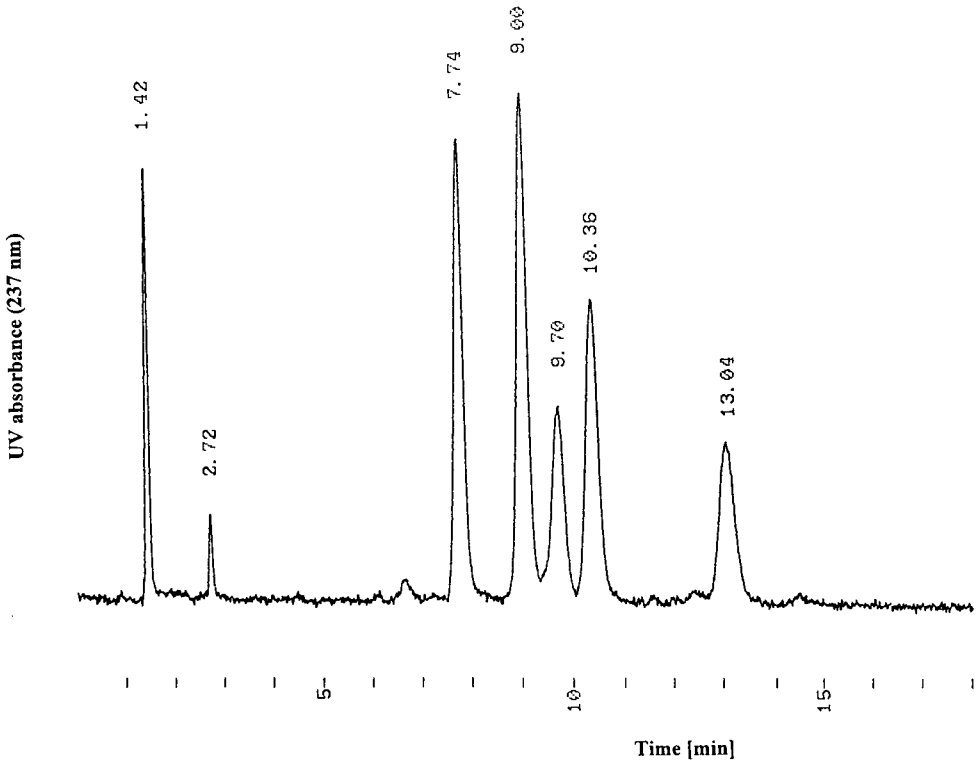


Figure 2. Chromatogram of the derivatives of EG, 1,2-PG, 1,3-PG, and 2,3-BG measured with the UV detection at 237 nm and concentrations of 10 mg/L. Retention times of derivatives (in min): 7.74, EG; 9.00, benzyl alcohol (internal standard); 9.70, 1,3-PG; 10.36, 1,2-PG; 13.04, 2,3-BG. HPLC conditions: column Capcell Pack C18 (150 × 1 mm), mobile phase 55% acetonitrile−water, flow rate 50 $\mu$L/min, and injection volume 1 $\mu$L.

Table 2. Statistical Parameters of the Calibration Curves for Dibenzoyl Derivatives of Glycols with Electrospray Detection (20−1000 μg/L) and UV Detection at 237 nm (1−50 mg/L)

| | | | Electrospray Detection | | | | |
|---|---|---|---|---|---|---|---|
| compd | slope | intercept | $R^a$ | LOD (μg/L) | linear range (μg/L) | repeatibility[b] | SD[c] (%) |
| EG | 0.004 84 | 0.2769 | 0.8691 | 30 | 60−300 | 1.556 ± 0.107 | 6.88 |
| 1,3-PG | 0.002 82 | 0.0470 | 0.9976 | 50 | 100−1000 | 0.763 ± 0.048 | 6.29 |
| 1,2-PG | 0.017 50 | 0.2685 | 0.9901 | 20 | 40−300 | 4.707 ± 0.093 | 1.98 |
| 2,3-BG | 0.016 19 | −0.1988 | 0.9937 | 30 | 60−1000 | 3.810 ± 0.488 | 12.8 |
| | | | UV Detection | | | | |
| compd | slope | intercept | $R^a$ | LOD (mg/L) | linear range (mg/L) | repeatibility[d] | SD[c] (%) |
| EG | 0.1008 | −0.0010 | 0.9960 | 1 | 2−50 | 1.055 ± 0.036 | 3.41 |
| 1,3-PG | 0.0847 | 0.0550 | 0.9974 | 1 | 2−50 | 0.944 ± 0.014 | 1.48 |
| 1,2-PG | 0.1043 | −0.0198 | 0.9987 | 1 | 2−50 | 1.048 ± 0.031 | 2.96 |
| 2,3-BG | 0.1258 | −0.0393 | 0.9996 | 1 | 2−50 | 1.210 ± 0.048 | 3.97 |

[a] Correlation coefficient. [b] Five repeated measurements at a concentration of 250 μg/L. [c] Standard deviation. [d] Five repeated measurements at a concentration of 10 mg/L.

calibration curves were constructed by plotting the ratios of the peak areas of dibenzoyl glycols to the peak areas of the derivative of benzyl alcohol as the internal standard versus the concentrations of the glycol derivatives. The calibration curves are linear from 1 to 50 mg/L and pass through the origin. The LOD is defined at $S/N = 3$, and it is 1 mg/L for all glycols tested.

Figure 3 shows the chromatogram of a standard mixture containing 50 μg/L of each glycol with the ESI-MS in the SIM mode. The top chromatogram was recorded using SIM of the $m/z = 199$ ion (protonated phenol), the second chromatogram is SIM of the $m/z = 293$ and $m/z = 334$ ions (the $[M + Na]^+$ and $[M + Na + \text{acetonitrile}]^+$ ions of the derivative of EG), the third one is SIM of the $m/z = 307$ and $m/z = 348$ ions (the $[M + Na]^+$ and $[M + Na + \text{acetonitrile}]^+$ ions of the derivatives of 1,2-PG and 1,3-PG), and the last one is SIM of the $m/z = 321$ and $m/z = 362$ ions (the $[M + Na]^+$ and $[M + Na + \text{acetonitrile}]^+$ ions of the derivative of 2,3-BG).

The slopes, intercepts, and correlation coefficients of the calibration curves with the ESI-MS and the UV detection are listed in Table 2. The correlation coefficients are always higher than 0.995 for the UV detection and higher than 0.99 for the ESI-MS detection, except for the EG derivative. For the ESI-MS detection, the LOD defined at $S/N = 5$ is 10 μg/L for 1,2-PG, 15 μg/L for EG and 2,3-BG, and 25 μg/L for 1,3-PG. Values of LOQ at $S/N = 10$ are 2 times higher. The calibration curves are linear from LOQ to 300 μg/L for the derivatives of EG and of 1,2-PG and to 1000 μg/L for the derivatives of 1,3-PG and of 2,3-BG. The HPLC method with UV detection can be used for the determination of dibenzoyl derivatives of glycols in concentrations of 2−50 mg/L, where the calibration curves are linear with the relative standard deviation of the determination between 1.5 and 4%. However, for the aqueous matrixes with high salt concentrations, occurring in processing of nuclear waste materials, lower limits of detection are required. With electrospray mass spectrometric detection, the limits of detection are approximately 20−50 times lower than with UV detection. The dynamic range of the calibration curves is more limited than with the UV detection (from 40−100 to 300−1000 μg/L), and the relative standard deviation of the determination is slightly inferior (from 2 to 13%), but this level of precision seems acceptable at these low concentration ranges of glycols.

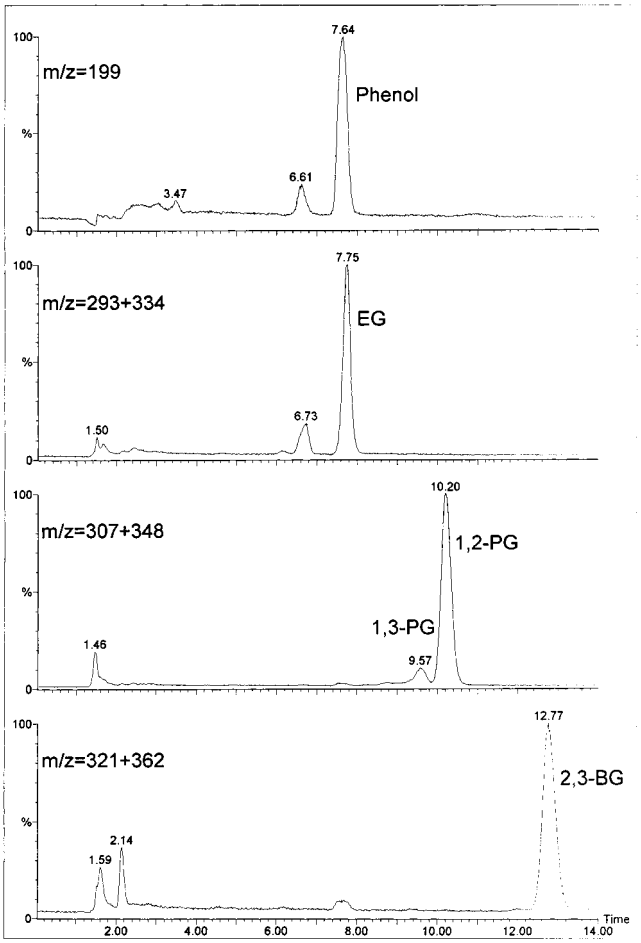


Figure 3. Chromatogram of the derivatives of EG, 1,2-PG, 1,3-PG, and 2,3-BG measured with the ESI-MS detection in the SIM mode at concentrations of 50 μg/L. HPLC conditions as for Figure 2.

The HPLC/MS method developed for the determination of EG, 1,2-PG, 1,3-PG, and 2,3-BG was used for the real samples containing approximately 100 g/L of salts. As discussed previously, no influence of the salt concentration was observed on the yield of derivatization. ESI-MS cannot cope with such high concentrations of salts due to signal suppression from ion pairing of the

Table 3. Concentrations of Glycols ($\mu$g/L) in Real Samples with High Contents of Salts Determined with ESI-MS Detection

| sample | EG | 1,2-PG | 1,3-PG | 2,3-BG |
|---|---|---|---|---|
| 1 | 45 | 55 | <50 | <30 |
| 2 | 210 | 160 | <50 | <30 |
| 3 | 910 | 170 | <50 | <30 |

analyte with the counterion of the salt and frequent contamination of the ion source, but the extraction of dibenzoyl derivatives separates them from all ionic compounds and hence the ESI-MS detection can be easily applied. The concentrations of glycols in three real samples analyzed are listed in Table 3. Samples 1 and 2 come from the interaction of water at neutral pH with a simple matrix (60% bitumen and 40% $NaNO_3$) with twice the integrated dose for the latter one. Sample 3 comes from the interaction of alkaline water with a matrix much more representative of the industrial process, which aside from bitumen and sodium nitrate contain other salts such as $NaSO_4$ together with cations such as cobalt, nickel, and others. The trends observed in terms of glycol content are coherent, i.e., more glycols mainly of low molecular weights with a more important integrated dose as well as with more alkaline water.

## CONCLUSIONS

Direct benzoylation of EG, 1,2-PG, 1,3-PG, and 2,3-BG in aqueous matrixes according to the Schotten−Baumann method makes possible the extraction of the dibenzoyl esters of glycols into a nonpolar solvent, which separates the derivatives from polar impurities and inorganic salts. The derivatization is fast and reproducible, and the derivatives of glycols show improved chromatographic behavior. A strong UV absorption of the dibenzoyl derivatives of glycols makes a sensitive UV detection possible. It also increases electrospray response with respect to free glycols because of an enhanced signal-to-noise ratio. The interferences are less probable in the mass range of the derivatives (270−298) than in that of the free glycols (62−90), where various interfering ions of low-mass adducts arising from the mobile phase occur. The method was used for the quantitative determination of glycols in real samples containing high concentrations of salts (approximately 100 g/L) with LOD 2−3 orders of magnitude better than in previous methods.

The derivatization with benzoyl chloride in the aqueous matrix could be also useful for the sensitive determination of other classes of compounds such as phenols and primary and secondary amines. The ESI-MS detection is also very sensitive for dibenzoyl derivatives of poly(ethylene glycol)s or poly(propylene glycol)s.

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