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Data Article

Data supporting the optimization of liquid chromatography tandem mass spectrometry conditions to analyze EPA-priority hormones and bisphenol A in water samples

Ken Goeury \(^a,b\), Sung Vo Duy \(^a\), Gabriel Munoz \(^a\), Michèle Prévost \(^b\), Sébastien Sauvé \(^a,\ast\)

\(^a\) Department of Chemistry, Université de Montréal, Montreal, QC, Canada
\(^b\) Department of Civil, Geological and Mining Engineering, École Polytechnique de Montréal, Montreal, QC, Canada

\*Corresponding author.
E-mail address: sebastien.sauve@umontreal.ca (S. Sauvé).

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This database presents the optimization of ultra-high-performance liquid chromatography electrospray ionization tandem mass spectrometry (UHPLC-MS/MS) for the analysis of EPA-priority endocrine disruptor compounds (13 hormones and bisphenol A). Various method parameters were tested and compared for improved sensitivity. Data related to the selection of the ionization source (heated-ESI vs. APCI) are presented, including optimization results of source parameters. Compound-dependent responses when varying the UHPLC mobile phase salt concentration of ammonium fluoride (\(\text{NH}_4\text{F}\)) are supplied. Details on the chromatographic gradient program and chromatographic data demonstrating the separation of \(\alpha\)-estradiol and \(\beta\)-estradiol are provided. In addition, we supply the details on mass spectrometry parameters under the optimized conditions, relative responses of quantification and confirmation MS/MS transitions (QT/CT), and number of points present in UHPLC-MS/MS spectra. The sample preparation and instrumental analysis procedures under the retained conditions are also described. The herein dataset supports the research "Analysis of Environmental Protection Agency priority endocrine disruptor hormones and bisphenol A in tap, surface and..."
1. Data

The following dataset includes 9 figures and 1 table that support the method optimization for the ultra-trace analysis of EPA-priority endocrine disruptors (hormones and bisphenol A). Mass spectrometry optimization is supported by 5 figure elements and one table. Figs. 1 and 2 show the acquisition reports for the optimization of MS/MS parameters (sheath gas, auxiliary gas, sweep gas, spray voltage, collision energy, precursor ion, predominating transitions), acquisition mode (separate or fast polarity-switching), and mobile phase types (including NH₄F concentration) for the detection of 13 hormones and bisphenol A at part-per-trillion levels. Fig. 3 presents the absolute area of each compound analyzed under different mass spectrometry conditions in separate acquisition mode vs. combined positive/negative fast polarity-switching mode. Fig. 5 highlights the normalized response of the targeted endocrine disruptor compounds related with the concentration of ammonium fluoride (NH₄F). Table 1 provides the
experimental details on compound-dependent MS/MS acquisition conditions. Chromatographic optimization is supported by 3 data files. Fig. 6 provides the UHPLC-MS/MS chromatographic peaks in point by point view while Fig. 7 shows chromatograms illustrating the separation of α-estradiol and β-estradiol. A summary of the chromatographic gradient program is presented in Fig. 8. The overall sample preparation is summarized in Fig. 9.

2. Experimental design, materials and methods

2.1. Mass spectrometry optimization

The tested mass spectrometry conditions are also described in our related research [1]. The herein data presents complementary information on the optimization steps for sheath gas, auxiliary gas, sweep gas, and the spray voltage (Fig. 1). Optimization of the product ion signal and the precursor ion signal was conducted, as was the optimization of collision energy (Fig. 2). The experimental design for the investigation of ionization source type and mobile phase conditions was established based on literature precedent [2–4]. Fig. 3 presents the variation of signal intensity depending on the selected source, atmospheric pressure chemical ionization (APCI) or heated electrospray ionization (heated-ESI), in combination with different mobile phases: H₂O/MeOH/NH₄F (20 mM) or H₂O+0.1% HCOOH/MeOH. The comparison of signal intensity obtained with polarity-switching ionization mode vs. separate mode acquisition is supported by Fig. 4. As discussed in our related study [1], the concentration of ammonium fluoride (NH₄F) in the LC mobile phase was optimized. The concentration of NH₄F was investigated at 6 levels (0–20 mM; concentration in line C), and normalized compound-dependent responses are illustrated in Fig. 5. Mass spectrometry parameters with the optimized method are provided in Table 1, which also includes details on relative responses of quantification and confirmation MS/MS transitions (QT/CT ratios).

![Fig. 1. Acquisition reports for the optimization of sheath gas, auxiliary gas, sweep gas and spray voltage using the heated-ESI source with H₂O/MeOH (50/50 v/v) as mobile phase for progesterone. The y-axis represents the intensity (counts/sec) while the x-axis represents either the gas flow in arbitrary units (Sheath_P, Aux_P, and Sweep_P) or the spray voltage (Spray_V).](image-url)
2.2. Chromatographic performance

In accordance with U.S. EPA criteria we verified that each UHPLC-MS/MS chromatographic peak had a minimum of 10 data points (Fig. 6) [3]. The separation of α-estradiol and β-estradiol isomers is illustrated in Fig. 7. A summary of the gradient program used in the optimized on-line SPE – UHPLC-MS/MS method is provided in Fig. 8.

**Fig. 2.** Acquisition reports for the optimization of precursor ion signal, fragment ion signal and the corresponding collision energy using the heated-ESI source with H2O/MeOH (50/50; v/v) as mobile phase for progesterone. The y-axis represents the intensity (counts/sec) while the x-axis represents either the mass-to-charge (m/z) ratio or the voltage for the collision energy (CE).
Fig. 3. Absolute area of each compound analysed under different source types, APCI or heated-ESI (HESI), under the negative mode (left) and positive mode (right) acquisition. The tested mobile phases were as follows: (1) H₂O+0.1% HCOOH/MeOH and (2) H₂O/MeOH/NH₄F(20mM). The absolute area is indicated in arbitrary units (A.U.).

Fig. 4. Absolute area of each compound analyzed under different mass spectrometry conditions, using the heated-ESI source for separate acquisition mode vs. combined positive/negative fast polarity-switching mode. Compounds are arranged according to their ionization (left panel: negative mode compounds; right panel: positive mode compounds). The absolute area is indicated in arbitrary units (A.U.).

Fig. 5. Normalized response of the targeted endocrine disruptor compounds, when the concentration of ammonium fluoride (NH₄F) was varied in the range 0–20 mM (concentration in solvent C). For this test, we used the heated-ESI source in positive/negative polarity-switching mode.
2.3. Sample preparation and analysis

The overall procedure for sample preparation is presented in Fig. 9. The sampling steps were previously described [5]. Briefly, at each sampling site the sample was collected in a 1L amber glass bottle and amended with 1 mL of NaCl aqueous solution at 116 g L⁻¹ and 1 mL of Omadine salt (2-mercaptopyridine-N-oxide sodium salt) aqueous solution at 70 g L⁻¹. The samples were then capped, hand-shaken, and stored at 4 °C until arrival at the laboratory. The samples were passed through 0.3 μm glass fiber filters (GFF-75). The samples were then spiked with the isotope-labelled internal standards (IS) mixture (corresponding to an added quantity of 1.25 ng for each IS) and submitted to high-speed agitation (30 seconds, 3200 rpm) using a LP Vortex mixer from Thermo Scientific. The different types of samples, including tap water, surface water, and wastewater [1], were then analyzed as follows.

The samples were submitted to on-line solid phase extraction (SPE) coupled to ultra-high-performance liquid chromatography tandem mass spectrometry (UHPLC-MS/MS) through a polarity-switching ionization source. A total analysis time of 15.5 minutes per sample was achieved.

The sample delivery system comprised a dual switching-column array. In-loop sample injection was performed with an HTC thermopal autosampler (CTC Analytics AG, Zwingen, Switzerland). The column-switching system [6] was composed of two-position six-port and ten-port valves (VICI Valco Instruments Co., Inc., Houston, TX, U.S.A.). The injection volume was set at 10 mL. An Accela 600 quaternary pump (Thermo Fisher, San Jose, CA, U.S.A.) was used to transfer the sample from the loop to
the on-line enrichment column. On-line SPE was achieved using two Hypersil Gold aQ C18 columns (20 mm × 2 mm, 12 μm particle size) connected in series. The on-line SPE mobile phases were HPLC-water with 0.1% formic acid (A) and methanol (B). The gradient program (Fig. 8) comprised three

Fig. 6. UHPLC-MS/MS chromatographic peaks in point by point view, illustrated for quantification and confirmation MS/MS transitions of ethinylestradiol (left) and testosterone (right). Each compound was verified to reach the U.S. EPA criterion that recommends a minimum of 10 points per peak [3].

Fig. 7. UHPLC-MS/MS chromatograms illustrating the separation of α-estradiol and β-estradiol isomers.
sequential steps: i) the on-line SPE loading (at 1500 \( \mu \)L min\(^{-1} \)) and washing step; ii) the elution of analytes and separation onto the analytical column; and iii) the conditioning of the analytical column and on-line SPE column prior to the following injection. The injection syringe and injector were washed with a 1:1:1 ACN:MeOH:IPA mixture and with HPLC-water containing 0.1% HCOOH prior to the next injection.

An Accela 1250 quaternary pump (Thermo Finnigan, San Jose, CA, U.S.A.) was used for sample elution from the enrichment column and subsequent separation on the analytical column. Analyte separation was performed using a Thermo Hypersil Gold C18 column (100 mm × 2.1 mm, 1.9 \( \mu \)m particle size) from Thermo Fisher Scientific (San Jose, CA, U.S.A.). The analytical column was thermostated at 55 °C and the mobile phases flow rate set at 500 \( \mu \)L min\(^{-1} \). The analytical mobile phases were HPLC-water (A), methanol (B) and HPLC-water with ammonium fluoride at 1mM (C). Details on the applied gradient program are supplied in Fig. 8.

**Fig. 8.** Summary of the gradient program for the optimized online SPE – UHPLC-MS/MS method (left panel: analytical pump; right panel: SPE pump). Analytical pump solvent lines were as follows: solvent A (H\(_2\)O), solvent B (MeOH), solvent C (NH\(_4\)F 1mM in H\(_2\)O). On-line SPE pump solvent lines were as follows: solvent A (HPLC-water with 0.1% HCOOH), solvent B (MeOH).

An Accela 1250 quaternary pump (Thermo Finnigan, San Jose, CA, U.S.A.) was used for sample elution from the enrichment column and subsequent separation on the analytical column. Analyte separation was performed using a Thermo Hypersil Gold C18 column (100 mm × 2.1 mm, 1.9 \( \mu \)m particle size) from Thermo Fisher Scientific (San Jose, CA, U.S.A.). The analytical column was thermostated at 55 °C and the mobile phases flow rate set at 500 \( \mu \)L min\(^{-1} \). The analytical mobile phases were HPLC-water (A), methanol (B) and HPLC-water with ammonium fluoride at 1mM (C). Details on the applied gradient program are supplied in Fig. 8.

**Fig. 9.** Summary of the sample preparation procedure for surface water.
The TSQ Quantiva triple quadrupole mass spectrometer (Thermo Scientific, Waltham, MA, U.S.A.) was coupled to a heated electrospray ionization source (heated-ESI), operated in fast polarity-switching mode. Source parameters under the optimized conditions were as follows: sheath gas (60 arbitrary unit), auxiliary gas (15 arbitrary unit), sweep gas (0 arbitrary unit), ion spray voltage (+3kV or -3kV, polarity-switching), capillary temperature (350 °C), vaporizer temperature (400 °C). The scan time was set at 20 ms. The first and third quadrupole (Q1 and Q3) were set at unit resolution (0.7 Da FWHM). The collision gas pressure in the collision cell (q2) was fixed at 1.5 mTorr. The analyzer was operated in selected reaction monitoring (SRM) mode, and two MS/MS transitions were monitored for each compound [1]. Compound-dependent MS/MS parameters with the retained method are provided in Table 1.

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Transparency document

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