

High throughput analysis of some endocrine disrupting compounds (EDCs) in solid matrices by LDTD-MS/MS

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Overview

The development of a high-throughput method for the analysis of 16 endocrine-disrupting substances in environmental solid matrices has been investigated. The rapid method is based on the laser diode thermal desorption-atmospheric pressure chemical ionization (LDTD-APCI) coupled to tandem mass spectrometry (MS/MS). The method was tested and validated in two different solid matrices and its performance was evaluated by estimation of extraction recovery, linearity, precision, and detection limits.

The results for real environmental samples analyzed with the proposed method are also illustrated.

Environmental context and objectives

Among the group of endocrine disrupting compounds, natural and synthetic estrogens are considered the most potent estrogenic compounds [1]. The potential effects to human health and the ecological impacts of these natural and synthetic hormones are a growing concern, and have recently become the focus of scientific research [2, 3]. Parabens, the most common preservatives used in personal care products (cosmetics), in pharmaceuticals and food products and triclocarban (TCC), a common antibacterial chemical added to bath soaps can also alter hormonal activity in rats and in human cells representing a new category of endocrine-disrupting substance (EDS) [4, 5, 6].

Understanding the implication of various solid phases (i.e. sediment, sludge) in the fate of environmental of EDCs is absolutely needed in evaluating the environmental contamination by these compounds but implies the development of more effective methods for analyzing multiple components in large number of samples rapidly.

Few analytical methods for solid samples have been reported and were often adapted from those used for analyzing water samples. Time- and labor-consuming analytical procedures are usually needed for the sample preparation and preconcentration procedures required for the accurate determination of these substances.

To reduce sample preparation and analysis time, the development of a high-throughput method for the analysis of 16 EDCs (parabens, hormones and triclocarban) in solid matrices using LDTD-APCI-MS/MS has been developed. The method was tested in two types of solid matrices: sediment containing low concentrations of organic compounds in a diluted organic matrix, and municipal sludge cakes containing higher concentrations of selected compounds in a more complex matrix which can influence the performance of the analytical method.

Materials and methods

The structures of the selected compounds for this study are shown in Fig. 1.

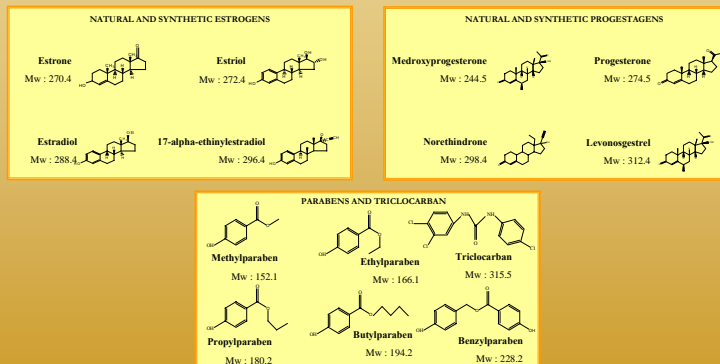
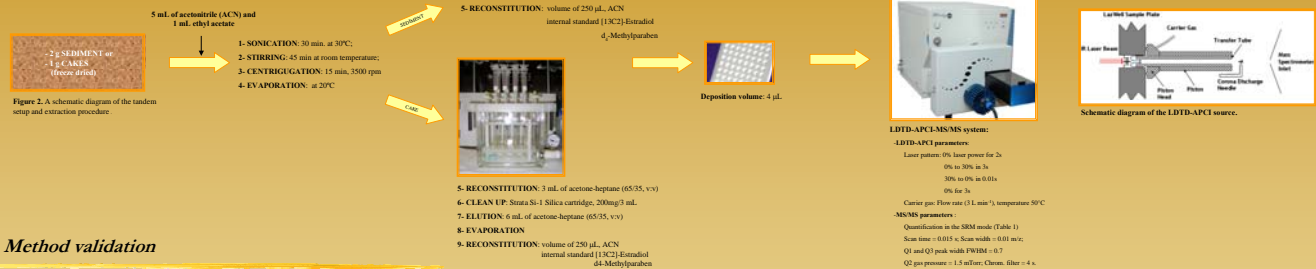


Figure 1. Molecular structures of selected compounds.

Instrument

The system consists of a TSQ Quantum Ultra AM Mass Spectrometer (Thermo Fisher Scientific, Waltham, MA, USA) with a LDTD-APCI ionization source (Phytronix, Quebec, Canada). A schematic diagram of the tandem setup and extraction procedure are described in Figure 2. The procedure for LDTD-APCI-MS/MS optimization is well described in Fayad et al. (2009) and was performed for all compounds [6].



Method validation

Table 1. Mass spectrometry optimized parameters for all selected compounds.

| Compound | Precursor ion (m/z) | Product ion (m/z) | CE (V) | Product ion (m/z) | CE (V) | Tube lens |
|----------------------|---------------------|-------------------|--------|-------------------|--------|-----------|
| Positive mode | | | | | | |
| Estradiol | 255.1 | 159.2 | 19 | 133.09 | 18 | 68 |
| 17-ethinyloestradiol | 279.1 | 133.2 | 19 | 159.0 | 25 | 46 |
| Norethindrone | 299.2 | 109.0 | 26 | 91.0 | 35 | 69 |
| Levonogestrel | 313.2 | 245.1 | 18 | 109.1 | 27 | 64 |
| Medroxyprogesterone | 345.2 | 123.0 | 25 | 97.0 | 23 | 74 |
| Progesterone | 315.2 | 109.2 | 24 | 97.1 | 20 | 65 |
| Triclocarban | 314.9 | 127.0 | 32 | 93.0 | 35 | 65 |
| Negative mode | | | | | | |
| Estril | 287.1 | 171.1 | 40 | 143.0 | 54 | 97 |
| Estrone | 269.1 | 145.1 | 41 | 143.0 | 57 | 84 |
| Methylparaben | 151.2 | 92.0 | 23 | 136.0 | 15 | 53 |
| Ethylparaben | 165.1 | 92.0 | 25 | 137.0 | 15 | 48 |
| Propylparaben | 179.0 | 92.0 | 25 | 136.0 | 18 | 53 |
| Butylparaben | 193.1 | 92.0 | 30 | 136.0 | 18 | 74 |
| Benzylparaben | 227.0 | 92.0 | 27 | 137.0 | 18 | 66 |

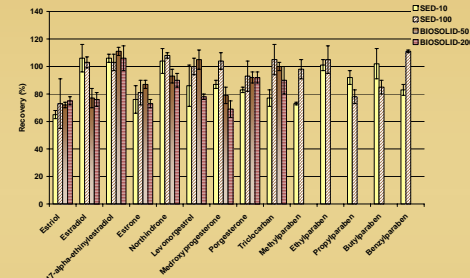


Figure 3. Recovery for all selected compounds in sediment matrix at 10 ng/g and 100 ng/g (SED-10, SED-100) and in municipal sludge cakes at 50 ng/g and 200 ng/g (BIOSOLID-50, BIOSOLID-200). The results are the mean of quadruplicate spikes, and the error bar lengths represent the relative standard deviations.

Environmental application

Municipal sludge cakes (Biosolid-I) were sampled at Montreal's sewage treatment plant (STP) (Quebec, Canada), the largest physico-chemistry treatment plant of the Americas which produce more than 28 000 metric tons of cakes per year. Sediments (Sediment-I) were also sampled from l'Îlet Vert situated within the dispersion plume of effluent discharged by Montreal's STP (Quebec, Canada). Thus, the level of contamination found in the Sediment-I will be depend to the wastewater outflow.

Table 3. Concentration (ng/g) of the selected compounds in sediment from l'Îlet Vert (Sediment-I) and municipal sludge cakes from the Montreal STP (Biosolid-I).

| Compound | SEDIMENT-I ng/g | BIOSOLID-I ng/g |
|----------------------|-----------------|-----------------|
| Estril | 18 ± 3 | 69 ± 3 |
| Estradiol | 103 ± 11 | 357 ± 3 |
| 17-ethinyloestradiol | 70 ± 6 | 255 ± 3 |
| Estrone | 16 ± 6 | 54 ± 3 |
| Norethindrone | 90 ± 9 | 106 ± 3 |
| Levonogestrel | 19 ± 5 | 53 ± 3 |
| Medroxyprogesterone | 29 ± 3 | 31 ± 3 |
| Progesterone | 172 ± 4 | 89 ± 3 |
| TCC | 16 ± 4 | 159 ± 3 |
| Methylparaben | 56 ± 7 | 72 ± 2 |
| Ethylparaben | 12 ± 2 | <LMD |
| Propylparaben | 15 ± 4 | 8 ± 1 |
| Butylparaben | 19 ± 3 | <LMD |
| Benzylparaben | n.d. | <LMD |

Conclusion

This proposed method for LDTD with APCI-MS/MS seems to be suitable for the rapid detection and quantification of some EDCs in solid matrices to overcome the use of liquid chromatography. Because of the simplicity of this system, generic method can be developed and applied for the high-throughput analysis of a wide variety of compounds.

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Table 2. Statistical parameters of calibration (equation, R²), limit of detection method (ng/g) and relative standard deviation (%) in sediment (SEDIMENT) and municipal sludge cake matrices (BIOSOLID).

| Compound | SEDIMENT | | | | BIOSOLID | | | |
|----------------------|------------------|----------------|---------------------------|----------|-------------------|----------------|---------------------------|----------|
| | Equation | R ² | MDL (ng.g ⁻¹) | R.S.D. % | Equation | R ² | MDL (ng.g ⁻¹) | R.S.D. % |
| Estril | y = 0.0065 0.122 | 0.990 | 3.9 | 4 | y = 0.0040 30.468 | 0.9750 | 10.0 | 13 |
| Estradiol | y = 0.0051 0.062 | 0.998 | 4.0 | 7 | y = 0.0140 7.085 | 0.9618 | 13.9 | 8 |
| 17-Ethinyloestradiol | y = 0.0051 0.114 | 0.991 | 2.1 | 2 | y = 0.0100 6.507 | 0.9871 | 12.0 | 8 |
| Estrone | y = 0.0121 0.086 | 0.995 | 2.2 | 2 | y = 0.0020 6.203 | 0.9960 | 9.2 | 11 |
| Norethindrone | y = 0.0084 0.266 | 0.993 | 2.0 | 5 | y = 0.0150 21.100 | 0.9691 | 16.6 | 14 |
| Levonogestrel | y = 0.0028 0.054 | 0.996 | 1.8 | 4 | y = 0.0140 15.215 | 0.9705 | 9.0 | 7 |
| Medroxyprogesterone | y = 0.0076 0.109 | 0.996 | 0.9 | 4 | y = 0.0120 2.907 | 0.9661 | 12.8 | 5 |
| Progesterone | y = 0.0074 0.175 | 0.991 | 6.5 | 8 | y = 0.0060 7.839 | 0.9879 | 13.1 | 5 |
| TCC | y = 0.0324 0.012 | 0.997 | 0.7 | 3 | y = 0.0090 1.649 | 0.9527 | 10.0 | 9 |
| Methylparaben | y = 0.0433 0.290 | 0.982 | 2.3 | 2 | y = 0.0070 6.485 | 0.9736 | 3.5 | 3 |
| Ethylparaben | y = 0.0710 0.128 | 0.993 | 1.8 | 7 | y = 0.0053 0.001 | 0.9554 | 6.4 | 8 |
| Propylparaben | y = 0.0230 0.357 | 0.990 | 1.9 | 5 | y = 0.0030 0.022 | 0.9888 | 2.8 | 1 |
| Butylparaben | y = 0.0451 0.233 | 0.972 | 1.6 | 9 | y = 0.0041 0.003 | 0.9874 | 2.9 | 4 |
| Benzylparaben | y = 0.0140 1.080 | 0.981 | 2.8 | 10 | y = 0.0015 0.015 | 0.9761 | 6.1 | 6 |

Equation and coefficient of determination for the calibration curve were performed in matrix concentration range from 100 ng/g for sediment and 100 ng/g for biosolid. Relative standard deviation of sediment and municipal sludge cake samples (n = 5) is depicted in a 50% concentration of 10 ng/g, the same way.

- ✓ All hormones were detected in the both matrices at concentrations ranging from 31 to 357 ng/g for biosolid-I samples and 18 to 172 ng/g for sediment samples (Table 3).
- ✓ Parabens were detected in sediment samples at concentration varying from 12 to 56 ng/g except for Benzylparaben whereas only methylparaben and propylparaben were found in biosolid sample at quantifiable concentrations, 72 and 8 ng/g, respectively (Table 3).
- ✓ The anti-bacterial compound, TCC, was present in the both matrices.