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Gas chromatography-mass spectrometry determination of o-phthalates in water coupled with liquid-liquid micro-extraction

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Esters of o-phthalic acid are the high toxic compounds. The plasticized polymers are the main source of the emergence of esters of o-phthalic acid in the environment. Gas chromatography-mass spectrometry method coupled with liquid-liquid micro-extraction pre-concentration was used for high sensitive determination of o-phthalates in water. The optimal extractant volume (10 μ L) was calculated from dependence of the impurities recovery on partition coefficient of impurities between the extractant (n-octane) and water. It was shown that the ultrasound assisted micro-extraction is an efficient method for pre-concentration of o-phthalates. Application of extract capillary collection solved the problem of the light extractant sampling. The following sources of systematic errors of the determination of o-phthalates have been found: Leaching of di-alkyl-o-phthalates from chromatographic septum; o-phthalates impurities in solvents; the hydrolytic lability of esters of o-phthalic acid. It was shown that the uncontrolled impact of these factors could lead to changes in the actual concentration of impurities determined at 1-2 orders of magnitude. The methods of accounting and elimination of systematic errors are proposed. Rayleigh distillation method was recommended for solvents purification. The storage time of water samples should not exceed three days. The lowering of o-phthalates leaching was achieved using merlin septa. The expanded uncertainty was calculated. It included precision, uncertainty of standards preparation, calibration, sample introduction, enrichment factor. The relative expanded uncertainty was at the level of 12.8–29.6%. The limits of detection and quantification of o-phthalates achieved were at the level of 10–10⁻⁶ mg L⁻¹ and were highly competitive with the best world results.

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Synthesis of two new derivatizing reagents and their application to separation of chiral drug

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Under appropriate reaction conditions of reaction time, temperature and solvent, the chlorine atoms in cyanuric chloride (2,4,6-trichloro-1,3,5-triazine; CC) can be substituted by nucleophiles in a controlled sequential manner, resulted into MCT (monochloro triazine) and DCT (dichloro triazine) based CDRs. Commercial availability and economic suitability makes the CC a more attractive starting material for the synthesis of CDRs. By these characteristics, synthesis of two MCT reagents, namely, N-(4-chloro-6-piperidinyl-[1,3,5]-triazine-2-yl)-L-Isoleucine; (CDR-1) and N-(4-chloro-6-piperidinyl-[1,3,5]-triazine-2-yl)-L-Methionine; (CDR-2) were carried out by nucleophilic substitution of one of the chlorine atoms by a piperidinyl group and the second with L-amino acids (as the chiral auxiliary). These reagents were characterized and used for derivatization of (RS)-isoprenaline (spiked in human plasma). The diastereomeric derivative were separated on a reversed-phase C18 column with a mobile phase consist of acetonitrile and 0.1% TFA under gradient mode from 35–65% of acetonitrile at a flow rate of 1.0 mL min⁻¹ and UV detection at 254 nm. The method was validation according to ICH guidelines. The separation mechanism and elution order of the diastereomeric derivative were proposed and supported by developing the geometry optimized lowest energy structures of the two diastereomers using a DFT based program, Gaussian 09 Rev. A.02 and hybrid density functional B3LYP with 6-31G basis set. In L-(R)-diastereomer, the bulky moieties, alkyl group on the stereogenic center of amino acid (present in the CDR), and phenyl group on stereogenic center of Ipn, are oriented on the same side with respect to triazine moiety, i.e., cis orientation. In L-(S)-diastereomer, these groups are oriented in a manner anti to each other with respect to triazine moiety and thus have a trans-type arrangement. Therefore, being less hydrophobic, it is L-(S)-diastereomer which eluted before its counterpart.

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