GC/MS/MS ANALYSIS OF URINARY METABOLITES OFORGANOPHOSPHORUS PESTICIDES.

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More than 75% of all existing Organophosphorus (OP) pesticides on the market are metabolised by hydrolysis in the human body to form up to six phosphorus containing hydrolysis products - Dimethyl Phosphate (DMP), Dimethyl Thiophosphate (DMTP), Dimethyl Dithiophosphate (DMDTP), Diethyl Phosphate (DEP), Diethyl Thiophosphate (DETP) and Diethyl Dithiophosphate (DEDTP). The analytical GC-MS/MS procedure for the determination of these metabolites in human urine is described.
Urine was fortified with Dibutyl Phosphate used as an Internal and Surrogate standard, and after lyophilization was derivatized with Pentafluorobenzyl Bromide reagent. Derivatives were analysed on triple stage quadrupole Mass-Spectrometer in parent-daughters experiment in NCI mode, monitoring Dialkyl Thiophosphate, Dialkyl Dithiophosphate and Dialkyl Phosphate ions as a parent ions and 2 ions from each as their break down products Fig1.
The calibration curve was linear up to 100 ppb for each analyte made up in acetonitrile and urine. The instrument detection limits for all analytes were 0.3-1 ppb depending on compound.
This method can be used for monitoring OP pesticide exposure in Occupational[1,2] and Environmental settings and offers considerable advantages in convenience and sensitivity over the determination of cholinesterase levels in blood.

No	Analyte	Parent Ion	m/z	Daughter Ions			
				Ion 1	m/z	Ion 2	m/z
Phosphates							
1	DMP	$[(CH_3O)_2PO_2]^-$	125	$[(CH_3O)PO_3]^-$	110	$[PO_3]^-$	79
2	DEP	$[(C_2H_5O)_2PO_2]^-$	153	$[(C_2H_5O)PO_3]^-$	125	$[PO_3]^-$	79
Thiophosphates							
3	DMTP	$[(CH_3O)_2PSO]^-$	141	$[(CH_3O)PO_2S]^-$	126	$[PO_2S]^-$	95
4	DETP	$[(C_2H_5O)_2PSO]^-$	169	$[(C_2H_5O)PO_2S]^-$	141	$[PO_2S]^-$	95
Dithiophosphates							
5	DMDTP	$[(CH_3O)_2PS_2]^-$	157	$[(CH_3O)POS_2]^-$	142	$[POS_2]^-$	111
6	DEDTP	$[(C_2H_5O)_2PS_2]^-$	185	$[(C_2H_5O)POS_2]^-$	157	$[POS_2]^-$	111

Fig. 1

1. Nutley, B.P., Cocker, J. Biological Monitoring of Workers occupationally exposed to Organophosphorus Pesticides. Pestic.Sci., 1993 ,38 ,315-322.

2. Peterson, J.C. Improved analysis of the Alkylphosphate Metabolites of Organophoshate Pesticides in Human Urine. International Symposium on Biological Monitoring in Occupational and Environmental Health, 11-13 September 1996 Espoo, Finland. Ed.: A.Aitio et al., ISBN 951-802-136-8, Finnish Inst. Occup. Health, Helsinki 1996.