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**Analysis of herbicides and pesticides in environmental water samples by gas chromatography-tandem mass spectrometry, both in their intact forms and as trimethylsilyl (oxime) ether/ester derivatives**

Pesticides and herbicides being used in the agriculture provide increase in the quality and quantity of products being obtained from it but if they are being applied without control on how it is done or how much is used than they do more harm than benefit to the environment. As in many other countries agriculture has always been one of the main occupations in Turkish Republic of Northern Cyprus and although the pesticides use has allowed for a more productive farming, their uncontrolled market and overuse has increased contamination, harming the environment [1]. Due to this the pesticides will be assessed as the extractions from soil, water, and agricultural products from respective sites in the island will be used in this study.

For the analysis Gas Chromatography – Tandem Mass Spectrometry (GC-MS/MS), with its common use in evaluation of pesticide and herbicide residues since it provides with high sensitivity, selectivity and quality in the process, is to be used for pesticide and herbicide residues control [2-4]. In order to insert the planned groups of pollutants into the existing multi-residue analysis system which are mainly obtained through previous research articles, different pesticides and their corresponding conditions will be examined.

Through various studies which have been conducted on pesticide and herbicide production along with their usage in agriculture, effects and toxicities on environment and living organisms [5-7], the starter pesticide has been selected as glyphosate (N-(phosphonomethyl)glycine). Prior to this pesticide, Carbaryl and Pirimiphos-methyl were analysed as introductory practical training. Three main articles were chosen as references for conducting the analysis glyphosate. Introductory investigations on this selected pesticide, with and without derivatization while relating their optimum responses were studied.

In this study the GC-MS/MS used for the analysis was GC-4000 type with MS Ion Trap detector in Full Scan Acquisition mode for Glyphosate with *N-tert*-Butyldimethylsilyl-N-methyltrifluoroacetamide (MTBSTFA). GC-240 model was used for measurements with the other reagents as seen in the Tables 1 and 2. Its stock solution was prepared with distilled water and a range of 0.2-2 ng was chosen as the GC injection for readable peaks. Four separate derivatization reagents were used; N-Methyl-N(trimethylsilyl) trifluoroacetamide (MSTFA), N,O-Bis(trimethylsilyl)trifluoroacetamide (BSTFA), Bis(trimethylsilyl)amine (HMDS) with Trifluoroacetic acid (TFA) and MTBSTFA. According to the first analysis, it can be seen that silylation alone has yielded better results than oximation and silylation combined. Rest of the analyses were completed accordingly. The best responses in the overall were achieved with MTBSTFA (Table 1) with glyphosate and its derivative, tris-butylmethylsilyl (ions: 454, 511, 253 and 352). MSTFA was the next best reagent and along

with BSTFA they had given double peaks for 3-TMS and 4-TMS derivatives. The values were too low compared to the MTBSTFA (Table 2).

In order to distinguish the optimum conditions, a range of temperatures and heating time intervals for derivatization with these reagents were checked; at ambient temperature, 70-80-100-120°C and for 15-30-60-90-120 minutes were taken as the basis [7-8]. The time and temperature combinations have shown variations within their own sets and between the sets. At ambient temperature, 70 and 120°C, the obtained values are significantly lowered compared to 80 and 100°C ones or inconsistent. Between the latter two, derivatization at 100°C, for 30 minutes has shown the optimum response per injection values. Although 15 minutes at the same temperature yields similar results, its relative standard deviation is higher. Any time longer than that decreases the peak area. At 80°C, the time for derivatization is needed to be at least 60 or 120 minutes and even then, it remains low. Hence the optimum temperature for glyphosate derivatization is decided as 100°C for 30 minutes.

A rerun of the tests were conducted after five and seven days on the derivatized samples to check whether the refrigerated storage was sufficient but the samples has shown degradation within these time intervals (Table 1). The only way to avoid decomposition is to run the samples through GC-MS/MS directly after the silylation process.

The conclusion achieved is that for maximum efficiency glyphosate should be derivatized at 100°C for 30 minutes with MTBSTFA and analyzed immediately. As further studies regarding glyphosate, its limit of quantitation values (LOQ) depending on the acquisition protocol applied, currently full scan; Extraction studies and optimizations as a function of the solid phase extraction (SPE) procedure; recovery optimization, in the light of LOQ phenomena will be conducted.

Throughout this year I have taken two courses and a laboratory practice. First course was held in the first term by Prof. Sergio Caroli, focusing on the advance spectrometry techniques in Antarctica, environmental research samples such as hair or car pollutants and Uranium generally. The second course and laboratory was held by Dr. Viktor Mihucz called the Food Analysis and it was about the analytical chemistry side of food and food industry, the methods of extraction and detection for specific matter in food samples and general applied chemistry in food science which has provided me with good laboratory practice along with analytical report writing as well as supporting my knowledge which has been lacking in the food analysis subject.

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**Table 1** Derivatization study of Glyphosates: response values obtained from model solutions (27000 pg of each), depending on the silylating agent, determined on the basis of their selective fragment ions (SFIs) by gas chromatography mass spectrometry (GC-MS), as their trimethylsilyl and or *terc*.butyldimethylsilyl(*t*.BDMS) (oxime) ether derivatives; MTBSTFA as reagent. Conducted on the instrument GC-4000.

Derivatization conditions ⇒ Derivatizaion time, min ↓		Integrator units /injected (2-40) pg for glyphosate				
		MTBSTFA				
		Av <sup>a</sup>	RSD%	Av <sup>b</sup>	RSD%	RSD% (Av <sup>a</sup> + Av <sup>b</sup> )
Ambient T. 60		5089	15			
Ambient T. 120		7363	0.04	6997	0.91	4
70 °C*	90	44527	1.96			
80 °C (2013.05.22)	15	19845	5.15	19815	21	1.33
	30	19933	30	18247	8.74	6.24
	60	23391	7.9	17902	0.4	19
	120	23560	0.2	18829	3.51	35
100 °C (2013.04.17)	15	21893	10	19308	17	8.87
	30	25276	1.50	20663	5.23	14
	60	21800	4.25	18215	6.35	13
	120	19556	0.87	13725	15	25
100 °C (2013.05.23)	15	26481	19	14141	6	43
	30	26277	2.79	15711	4.59	36
	60	22238	0.21	14984	7.91	28
	120	12939	13	6792	19	44
120 °C (2013.04.02)	30	25411	-			
	60	11218	-			
	120	4013	-			

Indications: Av<sup>a</sup> = analysis immediately after dilution; Av<sup>b</sup> = 5 days later

\* = Both oximation and silylation was done.

**Table 2** Derivatization study of Glyphosate: response values obtained from model solutions (27000 pg of each), depending on the silylating agent, determined on the basis of their selective fragment ions (SFIs) by gas chromatography mass spectrometry (GC-MS), as their trimethylsilyl and or *tert*.butyldimethylsilyl(*t*.BDMS) (oxime) ether derivatives; MSTFA, BSTFA and HMDS & TFA as reagents. Conducted on the instrument GC-240.

Derivatization conditions ⇒ Derivatizaion time, min ↓		Integrator units /injected pg for glyphosate					
		MSTFA					
		Av <sup>a</sup>	RSD%	Av <sub>3tms</sub>	RSD%	Av <sub>4tms</sub>	RSD%
Ambient t. 60		21914	4.52	5384	2.42	16545	5.07
80 °C	15	21402	1.82	6093	4.06	15322	4.28
	30	21382	3.13	6103	3.55	15281	5.79
	60	22816	9.02	4942	16	17870	7.04
	60 <sup>(2nd)</sup>	28468	3.82	8046	11	20431	0.74
	90	30886	2.46	9806	1.4	21080	4.26
	120	21176	2.86	5159	6.65	16071	1.64
100 °C	15	23642	3.72	9388	6.68	17254	2.62
	30	30168	2.45	10829	5.93	19338	0.51
	60	24488	3.07	7632	2.37	16856	3.38
	120	16643	2.87	5008	4.04	11635	2.36
120 °C	30	17443	-				
	60	18624	-				
	120	16586	-				
		BSTFA					
Ambient t. 60		3007	8.44	2837	9.51	173	7.42
80 °C	15	10691	109	19283	5.67	438	4.85
	30	24274	1.90	22608	1.94	1669	1.02
	60	22745	0.73	20871	1.07	1877	2.72
		HMDS+TFA					
		Av <sup>a</sup>	RSD%				
Ambient t.* 15		2122	30				
70 °C*	90	5993	39				
70 °C*	90	6580	7.18				
70 °C	90	15915	6.70				
80 °C	15	3595	0.62				
	30	2720	1.78				
	60	447	78				

Indications: as in Table 1, as well as: Av<sup>3tms</sup> = 3-TMS peak values; Av<sup>4tms</sup> = 4-TMS peak values.