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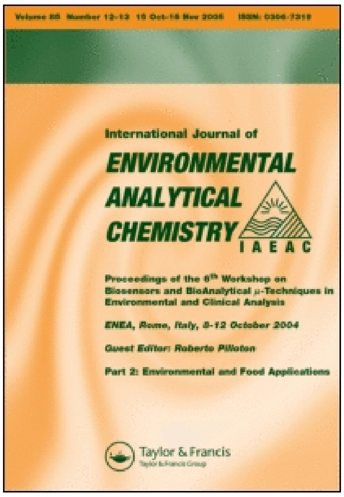

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The influence of mercury(II) on the extraction efficiency of herbicides from water

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In this work, the effect of Hg(II) on the extraction efficiency of triazine and phenylurea herbicides from water samples was tested. The results showed that in the presence of Hg(II), the recoveries of the *s*-triazine herbicides (except hexazinon) from styrene divinylbenzene (SDVB) cartridges were significantly reduced using acetonitrile as the elution solvent, whereas acidified methanol quantitatively eluted all the herbicides. Consequently, the loss in the recoveries was not due to degradation of the compounds but rather due to irreversible adsorption onto the resin. The adsorption is probably due to ternary complex formation between the compounds, Hg(II) and the polymeric resin. The chemical structure and the basicity of the compounds affected their interaction with Hg(II). When using octadecyl (C18) cartridges, only atraton was affected. Mercury did not affect the liquid–liquid extraction of the herbicides. The findings suggest that acidic methanol is a suitable elution solvent of *s*-triazines from mercury-loaded water samples.

Keywords: Mercury; HPLC; Triazine herbicides; Phenylurea herbicides; Stability; Complex formation

1. Introduction

In the past, many US Environmental Protection Agency (US EPA) drinking-water methods used mercuric chloride to minimize microbial growth and preserve water samples for the analysis of pesticides [1]. However, due to the known negative aspects of mercury (high toxicity and degradation potential of pesticides), the US EPA recently conducted stability studies to find suitable alternative preservatives [2–4].

In several studies, the ability of mercury(II) to degrade mainly organophosphorous [1, 5–7] or triazine [8] biocides in water solutions is reported. During the initial 14-day storage stability study of the US EPA National Pesticide Survey, 26 of 147 target

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analytes had 100% loss in recovery, which was probably due, in some cases, to preservation with mercuric chloride [1, 3]. Crescenzi *et al.* [6] reported up to 100% loss for 14 of the 34 pesticides stored in $HgCl_2$-containing river water samples in 21 days. Liu *et al.* [8] found that the Hg(II) ion catalyses the hydrolysis of Irgarol 1051, a methylthiotriazine used in antifouling paints, in water solutions.

Different studies indicate that metal cations are retained on common reversed-phase sorbents: the unreacted silanols of a C18 material could capture metal cations that serve as active sites for chelating compounds [9]. Metal cations are adsorbed on SDVB resins either on polar impurity surface sites (carboxyl, phenolic or similar groups) [10] or with non-ionic π–π interactions (complex formation) between ions and the aromatic resin backbone [11]. In addition, triazine herbicides form complexes with metals [12]. For example, atrazine forms complexes with cadmium, copper, and zinc but not with lead [13], and Irgarol 1051 forms complexes with Hg(II) [8].

In a recent study, different physical and chemical methods for the preservation of surface water samples containing triazine and phenylurea herbicides were examined [14]. Mercuric chloride was tested as a potential preservative according to the EPA preservation scheme. The samples were fortified with the preservative and the herbicides, extracted immediately with styrene-divinylbenzene cartridges and eluted with acetonitrile. The recoveries of the *s*-triazine herbicides were significantly reduced. The preservative did not affect the recoveries of the phenylurea herbicides. To our knowledge, there is no other relevant work in the literature reporting immediate loss of triazine compounds retained on a solid sorbent in the presence of Hg(II).

The aim of this study was to investigate the effect of mercuric chloride to the extraction efficiency of triazine herbicides from water samples. Taking into account the cited literature, two different hypotheses were tested: (1) A complex is formed between the sorbent, mercury, and the herbicides, resulting in irreversible retention of the compounds onto the cartridge; (2) mercury(II) catalyses the degradation of the compounds in the water solution or onto the solid-phase extraction cartridge. In order to test the two hypotheses, water samples were fortified with mercury and the herbicides, extracted with SDVB cartridges and eluted with different solvents (acetonitrile, methanol, and acidified methanol). The ability of EDTA to act as a masking agent to mercury(II) was also tested. Additionally, the effect of Hg(II) on the solid-phase extraction with C18 cartridges and the liquid–liquid extraction efficiency of the compounds was evaluated. The herbicide mixture included 16 important representatives from the chemical groups of the *s*-triazine and substituted phenylurea herbicides.

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2. Experimental

2.1 *Reagents and standards*

Merck (Darmstadt, Germany) supplied acetonitrile and methanol for gradient HPLC, mercury(II) chloride (*pro analysi*), and EDTA disodium salt (99%). Dichloromethane and acetic acid (HPLC-grade) were purchased by BDH (Poole, UK). HPLC-grade water was prepared in the laboratory using a MilliQ/MilliRO system (Millipore, Bedford, MA). Dr Ehrenstorfer (Ausburg, Germany) and ChemService

Table 1. Chemical groups of compounds, their water solubility, and pK_b.[a]

Compound	Chemical group	Water solubility (20 or 25°C) (mg/L)	pKb
Triazines			
Atraton	Alkoxy- alkylamino-*s*-triazine	1800 [15]	9.8 [16]
Atrazine	Chloro-alkylamino-*s*-triazine	33 [17]	12.32 [17]
Cyanazine	Chloro-alkylamino-cyanoalkylamino-*s*-triazine	170 [17]	12.9 [17]
Deisopropyl atrazine	Chloro-alkylamino-amino-*s*-triazine/metabolite	–	12.7 [16]
Desethyl atrazine	Chloro-alkylamino-amino-*s*-triazine/metabolite	–	12.7 [16]
Hexazinone	Symmetrical triazine with carbonyl in position 2	33 000 [17]	12.9 [18]
Metamitron	Non-symmetrical triazine	1700 [16]	
Prometryn	Alkylthio-alkylamino-*s*-triazine	33 [17]	9.95 [17]
Propazine	Chloro-alkylamino-*s*-triazine	8.6 [17]	12.15 [17]
Simazine	Chloro-alkylamino-*s*-triazine	6.2 [17]	12.35 [17]
Terbuthylazine	Chloro-alkylamino-*s*-triazine	5 [19]	12.06 [20]
Phenylureas			
Chlorotoluron	Aryl-urea	70 [21]	
Diuron	Aryl-urea	42 [17]	
Linuron	Arylalkoxy-urea	75 [17]	
Metobromuron	Arylalkoxy-urea	330 [19]	
Monolinuron	Arylalkoxy-urea	735 [17]	

[a] The absence of a pK_b value for a chemical indicates that it is assumed that ionization cannot occur [17]. A dash (–) in the same field indicates that the compound is a base, but the value of pK_b was not found in the literature. A dash (–) in the water-solubility field indicates that a water-solubility value was not found.

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(West Chester, PA) supplied analytical standards of the 16 herbicides and degradation products (table 1). The purity of the standards ranged between 95.5 and 99.8%. Stock solutions of individual herbicides were prepared in methanol, at a concentration of 1 mg/mL, except simazine (0.5 mg/mL), and stored in the dark, at 4°C, for 3 months.

2.2 *LC instrumentation and analysis*

The LC system consisted of a 9012 pump, associated with a Polychrom 9065 diode-array detector (Varian, Walnut Creek, CA) and a Rheodyne 7161, 100 µL, loop injector (Rheodyne, Rohnert Park, CA). The wavelength of the detector was set at 220 nm for the determination of triazines and at 244 nm for the determination of phenylureas and hexazinon.

The column was a 4.6 mm × 15 cm (5 µm) Zorbax SB-C18 column connected to a Zorbax SB-C18 pre-column (Hewlett Packard, Palo Alto, CA). The column and pre-column were heated at 40°C with a block heater (Jones Chromatography, Hengoed, UK). The optimization of the separation of the mixture using a mobile phase consisted of acetonitrile–water and is described in detail elsewhere [22]. Briefly, the composition of the mobile phase changed from 10% to 100% acetonitrile in 40 min. The flow rate was 1.2 mL/min. The 16 compounds were separated in 22 min.

2.3 *AAS instrumentation and mercury analysis*

The concentration of mercury was measured in the inlet and outlet solution of the cartridges using cold-vapour atomic absorption spectrometry with a Perkin Elmer

4110ZL atomic absorption spectrometer equipped with an FIAS 400 and an autosampler AS-90. A 500 µL injection loop was used. The samples were loaded for 30 s (injection valve in FILL position) and measured for 20 s (with the injection valve in the inject position).

2.4 *Procedures*

In all the experiments, 100 mL of ultrapure water was extracted. The concentration of the spiked herbicides was 4 µg/L for each compound. Mercuric chloride in a nominal concentration of 10 mg/L was used to provide 37 µmol/L of Hg(II) in the water solution.

The first experiment was conducted to test possible interactions between mercury(II) and the herbicides during the solid-phase extraction. Ultrapure water was spiked with the 16 compounds and mercuric chloride, and mixed in an ultrasonic bath for 10 min. SDVB (500 mg, Envichrom-P, Supelco, Bellefonte, PA) and C18 cartridges (500 mg, Sep Pak Vac, Waters, Ireland) were activated using 10 mL of methanol and 10 mL of ultrapure water. The water sample was passed through the cartridges at a flow rate of 5–8 mL/min. The cartridges were dried for 5 min under a stream of air, and the herbicides were eluted three times with 2 mL of acetonitrile. The acetonitrile of the eluate was carefully evaporated under a stream of nitrogen, the dry residue was reconstituted with 1 mL of a mixture of acetonitrile/water 1/9 (v/v), and the solution was analysed with HPLC.

The solid-phase extraction procedure with the SDVB cartridges was repeated using the following elution solvents: acetonitrile and acidified methanol (acetic acid/methanol 2/8 v/v), in succession, methanol, and acidified methanol (acetic acid/methanol 2/8 v/v).

In order to check the liquid–liquid extraction efficiency of the compounds in the presence of mercury(II), ultrapure water was spiked again with the 16 compounds and mercuric chloride and mixed in an ultrasonic bath for 10 min. The water was extracted three times with 30 mL of dichloromethane; the dichloromethane phase was evaporated to 2 mL in a rotary evaporator at 35°C. The remaining solvent was evaporated carefully to dryness under a stream of nitrogen, and the dry residue reconstituted with 1 mL of a mixture of acetonitrile/water 1/9 (v/v) and analysed with HPLC.

The ability of EDTA to act as a masking agent to mercury(II) was tested by fortifying ultrapure water in succession with 50 mg/L of EDTA disodium salt, 10 mg/L of $HgCl_2$, and 4 µg/L of each of the compounds. The sample was extracted with SDVB cartridges and eluted with acetonitrile as described in the first experiment.

All the treatments were repeated three times. In all the experiments, treatment under the same conditions, without mercury(II), was included to compare the results. The least significant difference test (LSD) at the 0.05 level of significance (Statgraphics 4.0) was used to compare mean values.

3. Results and discussion

In a recent study, it was observed that the addition of mercuric chloride in water samples to preserve herbicides resulted in reduced recoveries for *s*-triazine

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Table 2. Recoveries of the herbicides (± relative standard deviation) extracted using C18 and SDVB cartridges and eluted with acetonitrile, with or without $HgCl_2$.

	Average recovery (RSD)			
Compound	C18, without $HgCl_2$	C18, with $HgCl_2$	SDVB, without $HgCl_2$	SDVB, with $HgCl_2$
Triazines				
Atraton	90.3 (11)	50.9 (43)	98.4 (3.3)	0.0 (–)
Atrazine	96.2 (3.3)	96.5 (6.7)	92.2 (5.7)	30.9 (11)
Cyanazine	102 (2.7)	102 (5.2)	97.3 (3.9)	11.4 (17)
Deisopropyl atrazine	71.7 (3.3)	74.0 (5.4)	96.7 (3.9)	34.9 (10)
Desethyl atrazine	100 (2.2)	98.4 (5.4)	98.4 (2.7)	19.3 (14)
Hexazinone	109 (3.4)	102 (7.7)	104 (7.2)	107 (6.6)
Metamitron	101 (3.0)	99.0 (4.5)	97.2 (5.4)	103 (9.9)
Prometryn	92.1 (6.8)	87.9 (6.1)	84.6 (8.3)	4.50 (61)
Propazine	100 (5.0)	92.6 (9.1)	94.2 (5.0)	23.3 (14)
Simazine	104 (5.4)	100 (6.3)	99.4 (5.7)	43.5 (12)
Terbuthylazine	87.4 (9.1)	89.0 (10)	80.7 (8.0)	40.8 (11)
Phenylureas				
Chlorotoluron	101 (5.1)	101 (4.8)	96.7 (4.4)	104 (5.4)
Diuron	103 (3.8)	102 (6.2)	95.2 (2.5)	103 (5.5)
Linuron	89.9 (5.5)	91.7 (8.5)	85.8 (14)	94.1 (6.6)
Metobromuron	90.8 (5.9)	91.2 (9.9)	89.7 (11)	98.1 (8.1)
Monolinuron	84.1 (14)	82.6 (15)	88.4 (11)	95.8 (12)

compounds [14]. The compounds were extracted with C18 and SDVB cartridges and eluted with acetonitrile, which is an effective solvent for the elution of triazines from both sorbent materials [23]. The recoveries of the compounds with or without the addition of mercury(II) are presented in table 2. In this table, it is shown that the presence of $HgCl_2$ did not affect the solid-phase extraction efficiency of the herbicides from C18 cartridges, except atraton. The recovery of atraton decreased (from 90 to 51%), and its precision deteriorated (relative standard deviation RSD = 43%) in the presence of Hg(II).

Mercuric chloride severely affected the extraction efficiency of the SDVB cartridges. The recoveries of the *s*-triazines, namely deisopropyl atrazine, desethyl atrazine, simazine, cyanazine, atraton, atrazine, propazine, terbuthylazine, and prometryn, were significantly lower (table 2). On the contrary, the recoveries of metamitron (non-symmetric triazine), hexazinone (*s*-triazine with carbonyl in position 2), and the phenylureas (chlorotoluron, monolinuron, diuron, metobromuron, and linuron) remained unaffected.

Mercury concentration was measured in the inlet and outlet of the cartridges (table 3). Almost all the Hg(II) was retained on the SDVB cartridge during the extraction of the water, and only a minute amount was detected in the outflow (0.11 μmol/L). Mackey [10] reported the adsorption of simple cations of copper, iron, and zinc onto polystyrene XAD-1 and XAD-2 resins, probably captured by polar impurity surface sites (carboxyl, phenolic, etc.) of the resin. Cecchi *et al.* [11] suggested that metal ions could be retained on a non-ionic SDVB based resin with π–π interactions (complex formation) between ions and the aromatic resin backbone. Since the modern SDVB cartridges are highly pure materials [24], and Hg(II) forms labile π-complexes with unsaturated and aromatic organic chemicals [25], the second retention mechanism seems reasonable.

Table 3. Measured concentrations (± relative standard deviation) of $HgCl_2$ in the inlet and outlet solutions of the cartridges.

	Concentration of Hg (RSD%) (μmol/L)
Inlet C18 or SDVB	36.1 (1.5)
Outlet C18	35.8 (1.5)
Outlet SDVB	0.11 (4.6)
Outlet SDVB in the presence of EDTA	36.5 (4.6)

Table 4. Recoveries of herbicides (± relative standard deviation) extracted from water containing $HgCl_2$ with SDVB cartridges and eluted in succession with acetonitrile and acidified methanol.

	Average recovery (RSD)		
Compound	Acetonitrile	Acidified methanol	Total
Triazines			
Atraton	0.00 (–)	107 (4.7)	107 (4.7)
Atrazine	31.9 (1.7)	67.1 (2.5)	99.0 (2.3)
Cyanazine	11.1 (4.8)	91.3 (2.9)	102 (2.2)
Deisopropyl atrazine	37.3 (2.0)	63.1 (1.4)	100 (1.6)
Desethyl atrazine	21.4 (4.7)	80.2 (5.9)	101 (4.3)
Hexazinone	108 (4.2)	0.0 (–)	108 (4.2)
Metamitron	112 (4.0)	0.0 (–)	112 (4.0)
Prometryn	2.20 (39)	81.1 (1.7)	83.3 (2.7)
Propazine	22.5 (5.6)	73.4 (3.0)	95.9 (3.5)
Simazine	43.2 (6.5)	58.2 (5.9)	101 (6.1)
Terbuthylazine	43.8 (1.6)	46.6 (2.5)	90.3 (1.2)
Phenylureas			
Chlorotoluron	105 (0.8)	0.0 (–)	105 (0.8)
Diuron	100 (12)	0.0 (–)	100 (12)
Linuron	90.8 (0.6)	0.0 (–)	90.8 (0.6)
Metobromuron	95.4 (2.8)	0.0 (–)	95.4 (2.8)
Monolinuron	95.7 (7.0)	0.0 (–)	95.7 (7.0)

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Taking into account the results and the literature cited, two hypotheses were made: the retained mercury(II) on the SDVB material either catalysed the degradation of the herbicides or promoted their irreversible adsorption onto the resin. In the following experiments, both hypotheses were examined.

At first, the SDVB cartridges were eluted with acetonitrile and acidified methanol in succession. As shown in table 4, acidified methanol removed the remaining amount of the compounds from the resin. The total recoveries were equivalent to the recoveries obtained with SDVB cartridges without mercury(II) (table 2). Nielen *et al.* [26] proposed that the acidification of the elution solvent could desorb chelated organic compounds onto stationary phases containing mercury(II). The results of table 4 support the hypothesis that the loading of the stationary phase with mercury(II) provides active sites for the adsorption of the triazines. Furthermore, the results prove that the compounds do not degrade in the water solution or onto the resin in the presence of mercury(II) during the experiment.

In addition to acetonitrile, the elution strength of methanol and acidified methanol using SDVB cartridges in the presence of mercury(II) was tested (table 5).

Table 5. Recoveries of herbicides (± relative standard deviation) extracted from water containing $HgCl_2$ with SDVB cartridges and eluted with acidified methanol and with methanol and acidified methanol in succession.

Compound	Average recovery (RSD)		
	Acidified methanol	Methanol	Methanol, re-elution with acidified methanol
Triazines			
Atraton	88.0 (3.9)	43.6 (33)	35.7 (57)
Atrazine	83.5 (7.2)	82.9 (7.3)	0 (–)
Cyanazine	88.3 (1.8)	97.1 (11)	3.8 (3.6)
Deisopropyl atrazine	89.3 (4.1)	95.8 (7.3)	0 (–)
Desethyl atrazine	92.2 (2.0)	89.0 (9.9)	6.6 (28)
Hexazinone	95.5 (3.6)	101 (12)	0 (–)
Metamitron	90.1 (14)	104 (7.1)	0 (–)
Prometryn	75.2 (13)	67.7 (13)	4.4 (70)
Propazine	82.5 (9.0)	78.4 (7.0)	0 (–)
Simazine	89.0 (6.7)	92.9 (10)	0 (–)
Terbuthylazine	73.0 (1.4)	71.4 (16)	0 (–)
Phenylureas			
Chlorotoluron	90.2 (11)	90.4 (5.0)	0 (–)
Diuron	87.5 (7.2)	100 (12)	0 (–)
Linuron	76.0 (12)	72.2 (16)	0 (–)
Metobromuron	81.5 (7.5)	72.7 (5.2)	0 (–)
Monolinuron	83.8 (5.4)	65.7 (6.6)	0 (–)

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Acidified methanol resulted in high recoveries for all the compounds. Methanol eluted all the compounds except atraton, indicating a stronger affinity between atraton and the loaded with Hg(II) sorbent. Methanol is a better solvent for the elution of the compounds compared with acetonitrile probably because it is a much more acidic solvent compared with acetonitrile (autoprotolysis constants, pK_s, of methanol 16.7 and acetonitrile 32.2 [27]). Thus, methanol interacts with the *s*-triazines much more effectively because these herbicides are weak bases (table 1).

In order to verify the hypothesis of complex formation between the SDVB resin, Hg(II), and the triazines, water samples were fortified in succession with EDTA disodium salt, $HgCl_2$, and the herbicides. EDTA and its salts have very high chelate-forming quotients with multivalent metal ions preventing it them from interacting with labile compounds [28]. After the extraction, the herbicides were quantitatively eluted with acetonitrile. All the mercury(II) of the sample was detected at the outflow of the cartridge (table 3). Thereby, EDTA forms complexes with mercury, which are not retained onto the SDVB cartridge.

Unlike SDVB, the C18 material did not significantly retain Hg(II). The concentration of mercury measured in the outflow of the C18 cartridges (35.8 μmol/L) was not statistically different to its concentration in the inflow (36.1 μmol/L) (table 3). The increased affinity of $HgCl_2$ for materials that possess aromatic moieties (SDVB sorbent) compared with alkanes (C18 sorbent) is indicated by its increased solubility to benzene (5 mg/mL) [29] and toluene ($\geq$2 mg/mL) [30], compared with hexane ($<$0.040 mg/mL) [30]. However, during the manufacture of a C18 sorbent, an amount of silanols remains unreacted due to steric effects. The percentage of the unreacted silanol groups is not exactly known. The end-capping procedure that follows aims to reduce the amount of unreacted silanols but cannot eliminate them [31]. Cecchi *et al.* [9] found that the unreacted silanols of a C18 material could serve as ion-exchange sites for metal cations.

Atraton exhibited highly variable recoveries in the presence of mercury(II) with acetonitrile (average recovery 51%, RSD 43%, table 2). Acidified methanol was tested as an elution solvent of the herbicides from the C18 material. Acidified methanol eluted quantitatively all the herbicides from the C18 cartridges. The recovery of atraton was $87.3 \pm 9\%$. A possible explanation for the variable recoveries of atraton with acetonitrile could be that a minute and variable amount of mercury was retained onto the unreacted silanols of the C18 cartridge with an ion-exchange mechanism [9] and provided active sites for the coordination of atraton.

The chemical structure of the compounds affected their interaction with mercury(II). The *s*-triazines with the general formula 2-*R*-4,6-alkylated diamino-*s*-triazine ($-R = -Cl$, $-OCH_3$, $-SCH_3$) were severely affected. On the contrary, hexazinon, a symmetrical triazine with carbonyl in position 2, metamitron, a non-symmetric triazine, and all the phenylureas, remained unaffected. Hance [12] proposed that transition metals coordinate with *s*-triazines via the nitrogen atoms of the diamino groups in positions 4 and 6.

Atraton interacted more strongly with mercury, compared with all the other herbicides: With the SDVB cartridges and acetonitrile, all of the atraton was retained on the cartridge (table 2), and it was the only compound which was not quantitatively eluted with methanol (table 5). In the case of C18 cartridges, only atraton was affected by the addition of mercury(II) (table 2). Atraton is the most basic compound of the mixture ($pK_b = 9.8$) (table 1). The basicity of the *s*-triazines depends on the substitution in position 2 of the molecule. Generally, methylthio-triazines and methoxy-triazines are more basic compounds than the chlorotriazines (table 1). Atrazine and atraton are identical molecules apart from the substitution in position 2. The interaction of atrazine with mercury was weaker than with atraton (tables 2 and 4). Likewise, prometryn has an identical structure to propazine apart from the substitution in position 2, which results in a greater basicity for prometryne and a stronger interaction with mercury than with propazine (tables 2 and 4). The substituted phenylureas do not exhibit basic or acidic properties, and none of them interacted with mercury.

The effect of $HgCl_2$ on the liquid–liquid extraction efficiency of the herbicides using dichloromethane was also examined. Ultrapure water spiked with the herbicides and $HgCl_2$ and extracted with dichloromethane. The recoveries of the compounds were not affected by the presence of the preservative. The results agree with the study of Munch and Frebis [1] who reported high recoveries of several triazine and phenylurea herbicides extracted with dichloromethane in the presence of mercury(II).

4. Conclusions

This work has shown that during the solid-phase extraction of *s*-triazine herbicides (except hexazinon) from Hg(II)-loaded water samples, a complex was formed between the polymeric SDVB sorbent, mercury(II) and the compounds. The complex was not broken by acetonitrile, while methanol quantitatively eluted all the compounds except atraton. Acidified methanol quantitatively eluted all the compounds. With C18 cartridges, the same phenomenon took place for atraton only. The chemical structure

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of the compounds and their basicity affected their interaction with mercury: the more basic the compound, the stronger the interaction with Hg(II) appears to be. The findings suggest that acidic methanol is a suitable elution solvent of *s*-triazines from mercury-loaded water samples. Mercury(II) did not influence the recoveries of the substituted phenylureas of the sample either with C18 or with the SDVB cartridges. The presence of Hg(II) during the liquid–liquid extraction did not affect the extraction efficiency.

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