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## The effect of freshwater UV-irradiation prior to resin preconcentration of trace metals

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### Abstract

Trace metal concentrations in natural freshwater samples are often below detection limits for determination by inductively coupled plasma-mass spectrometry (ICP-MS). This is especially so following size fractionation of the sample. Preconcentration is therefore necessary, and sorption on a chelating resin such as Chelex-100 is often used. In order to chelate metals strongly complexed with organics, the metal–organic association has to be severed. In this study, ultra violet (UV)-irradiation was used to oxidize organic matter in a humic acid reference solution, and in a natural sample spiked with Ag, Cd, Cu and Pb, where the recoveries of the metals were calculated. Except for Ag, recoveries of Cd, Cu and Pb increased significantly up to almost 100% after irradiation. If preconcentration on Chelex-100 is used, UV-irradiation appears to be an essential step in achieving accurate concentrations of organically chelated trace metals in freshwater. © 1999 Elsevier Science B.V. All rights reserved.

*Keywords:* UV; Resin preconcentration; Trace metal; Organic matter; Freshwater

### 1. Introduction

The low trace metal concentrations in freshwater, and particularly in the ultrafiltered fraction (<1 kDa), require a very sensitive method for measurement such as inductively coupled plasma mass spectrometry (ICP-MS) [1,2]. However, trace metal concentrations are generally close to the detection limits and a preconcentration step is necessary. This can be done by coprecipitation [3], solvent extraction [3,4], eva-

poration [5,6] or ion-exchange [7–9]. With the first three methods contamination is always possible due to the use of a large amount of reagent, or because of airborne particulate contamination during evaporation. Actually, ion-exchange separation with Chelex-100 chelating resin appears to be the best preconcentration method for trace metal determination. This resin possesses a high selectivity for polyvalent metal ions [10], without any retention of alkali and alkaline earth elements. The small volume of HNO<sub>3</sub> used for elution allows a high concentration factor (up to 50), low contamination, and provides a convenient medium for ICP-MS analysis. It is

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accepted that Chelex-100<sup>®</sup> resin retains metals in the free or labile forms, but the situation is less clear for metals associated with organic colloids [11]. In voltammetric analysis, interferences due to organic matter are eliminated by UV-irradiation [12,13], which has the further advantage of being clean and effective.

The aim of this paper is to check if the removal of metals from colloids by UV-irradiation will improve the efficiency of the resin preconcentration. Experiments were carried out by applying variable UV-irradiation on natural ultrafiltered freshwater and on a certified water reference standard.

## 2. Experimental

One hundred liter surface freshwater samples were collected from Lake Geneva (France – Switzerland) and were filtered on-line through a 1.2  $\mu\text{m}$  membrane filter (MSI), and a 1 kDa cross-flow cartridge (Millipore). The ultrafiltered fraction was acidified ( $\text{pH} < 2$ ) with suprapure  $\text{HNO}_3$  and was strongly enriched by the addition of metal ions to produce final concentrations between 4 and 5  $\mu\text{g/l}$  for Ag, Cd, Cu, Pb (hereafter designated as UFS). The solution was left for about 24 h for equilibration. Peat humic acid standard from IHSS was used to prepare an artificial organic rich solution. Certified water SRM 1643d was obtained from NIST and all chemical preparations were carried out in a class 100 clean laboratory.

The UV-irradiation apparatus consists of a 6 W UV lamp (ref: Philips TUV6W, 254 nm) with 4 m of PTFE tubing (1.63 and 0.81 mm for outer and inner diameter, respectively, Bioblock.) were wound at 2–3 cm distance around the lamp. The tubing was cleaned by successive washing with ultrapure 11% (v/v)  $\text{HNO}_3$ , and Milli-Q water ( $> 18 \text{ M}\Omega$ ). Each sample ( $\sim 40 \text{ ml}$ ) was introduced into the system by a peristaltic pump delivering a flow rate of 1 ml/min. This means that a cycle of UV-exposure lasts 40 min. Variable exposure times (from 1 to 3 cycles) were tested in order to check the efficiency of the irradiation.

Subsequently, the irradiated samples were preconcentrated on Chelex-100 (200–400 mesh, Bio-Rad Lab.). The resin column was made of FEP tubing (6.4 mm in diameter, 4 cm in length) closed by a polyethylene frit. Cleaning followed the same procedure as for the tubing. The conversion of the resin to

the ammonium form was achieved by equilibration with  $\text{NH}_4\text{OH}$  [14]. Finally, the resin was rinsed with Milli-Q water. The samples ( $\sim 40 \text{ ml}$ ) were buffered to  $\text{pH} = 5.3$  with ammonium acetate, and loaded into the column. Subsequently, the trace metals were eluted from the resin with 5 ml 9% (v/v)  $\text{HNO}_3$ . Both loading and elution were performed at a flow-rate of 1 ml/min. The whole resin preconcentration procedure took about 1 h.

Metal concentrations were determined by ICP-MS (POEMS1, Thermo Jarrell Ash, USA). Two sample introduction systems were used: a Scott chamber (Thermo Jarrell Ash, USA) and a Mistral<sup>®</sup> desolvating system (Fisons Instruments, USA). This latter system consisted of a heated spray chamber, where the solvent was first evaporated, and then condensed by a cooling system. This device improved the sensitivity by a factor of 2–10 compared to the Scott chamber. Typical operating conditions and detection limits are summarized in Table 1.

Fluorescence measurements were carried out with a Fluorolog 212 SPEX fluorimeter equipped with double monochromators for both excitation and emission. All spectra, both emission and excitation, were corrected for instrumental factors [15]. Measurements were performed in a 1 cm square fused silica cell thermostatically controlled at 20°C. The bandwidths for excitation and emission were both 4 nm, while wavelength increment and integration time were 0.5 nm and 0.5 s, respectively. In the present study, the 313 and 370 nm excitation wavelengths were chosen as they correspond to the humic substances fluorophores [16,17].

## 3. Results and discussion

### 3.1. Blank and efficiency of Chelex

Metal contamination, which may occur during the preconcentration process, has to be controlled because of the low concentrations of metals in natural samples [18,19]. The resin blanks were at least 10 times lower comparatively to the amount of metal usually contained in 40 ml of sample (Table 2).

The efficiency of the Chelex-100 resin (without any UV-irradiation) was checked using a multielemental standard solution (Merck IV) diluted to the concen-

Table 1

Instrumental parameters and limits of detection with both Meinhard/Mistral and cross-flow/Scott chamber introduction systems

Instrumental parameters		
RF power (W)	1250	
Plasma gas flow (l/min)	17	
Auxiliary gas flow (l/min)	1	
Nebulizer gas flow (ml/min)	0.65	
Sample uptake (ml/min)	0.9	
Metal	Limit of detection (ng/l)	
	Meinhard/ Mistral	Cross-flow/ Scott chamber
Ag	1.2	3.5
Cd	0.9	11.3
Cu	4.3	9.8
Pb	5.2	10.7

Limits of detections are calculated as three times the standard deviation of the blank signal (1% HNO<sub>3</sub>).

Table 2

Resin blank and resin efficiency

Metal	Resin blank (ng)	Resin efficiency (%)
Cd	0.6–1.4 (1.0)	92–102 (100)
Cu	0.5–1.0 (0.8)	97–106 (102)
Pb	0.1–0.3 (0.2)	94–108 (100)
Ag	0.4–0.7 (0.6)	97–108 (99)

For both parameters, the observed range is given and the mean values are given in parenthesis ( $n=6$ ). The efficiency was determined from a pure metal solution, free of organic matter.

trations of 0.2 µg/l for each metal. As shown in Table 2, trace metal recoveries range from 92% to 108%, with an average very close to 100% for each metal. This demonstrates that this method is fully satisfactory for an artificial solution.

### 3.2. Degradation of organic matter by UV-irradiation

It was demonstrated that metals associated with organic matter are not necessarily chelated/sorbed/bound to the resin, resulting in a resin efficiency decrease [11]. In natural freshwater, these organic compounds mainly consist of humic acids (HAs), which are characterized by the highest molecular weight, and fulvic acids (FAs), more abundant and

responsible of the largest part of the dissolved organic matter (DOM) fluorescence. Both HA and FA play an important role in metal complexation [20]. The degradation of these organic compounds will therefore improve the retention efficiency of the Chelex column. To achieve this degradation, variable doses of UV-irradiation were applied on two different solutions characterized by similar carbon content (~1.2 mg/l):

1. an artificial humic acid solution, in which if the UV-irradiation appeared to be efficient for HA, then it should also be efficient for smaller FA molecules;
2. an ultrafiltered freshwater sample (UFS as described above).

The effects of UV-irradiation on both of these solutions were monitored by fluorescence measurements (Fig. 1(a) and (b)). Actually, fluorescence is the sole sensitive technique to show the organic matter evolution with the irradiation cycles. Without UV-irradiation, both solutions give different spectra both in intensity and in wavelength of the maximum fluorescence emission. In fact, the peat humic acid solution is very rich in aromatic carbon and represents an extreme situation. In contrast, in natural water, FA and HA have lower molecular weights, inducing higher intensity and blue-shifted spectra. By increasing the number of UV-irradiation cycles, fluorescence intensities systematically decrease in both solutions, suggesting a progressive destruction of the fluorophores [21]. This degradation of HA and FA is almost totally achieved after two cycles.

### 3.3. Influence of UV-irradiation on trace metal preconcentration

A first set of experiments was carried out on the UFS solution. The effect of a pretreatment, consisting of (a) no UV, (b) UV, and (c) UV+H<sub>2</sub>O<sub>2</sub> addition, was evaluated for resin efficiency (Table 3). H<sub>2</sub>O<sub>2</sub> was tested because photooxidation may be accelerated using such a strong oxidant [22]. For both cases (b) and (c), one or two cycles of UV-exposure were carried out. Except for Ag, metal recoveries were low (82–89%) without UV. When UV or UV+H<sub>2</sub>O<sub>2</sub> were applied, the metal recoveries improved significantly ( $p<0.05$ ). One cycle of exposure appeared sufficient for Cd and Pb (efficiency close to 100%),

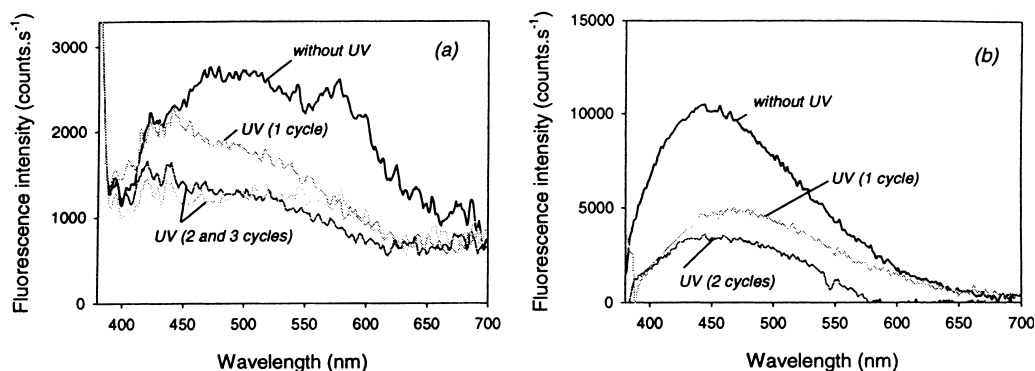


Fig. 1. Fluorescence emission spectra of (a) humic acid solution and (b) UFS at  $\lambda_{\text{ex}}=370$  nm.

Table 3

Trace metal contents (expressed in  $\mu\text{g/l}$ ) measured in UFS and SRM 1643d waters after different pretreatments (see text for details) and preconcentration on Chelex-100 resin

	Cd	Cu	Pb	Ag
<i>UFS solution</i>				
Expected values	4.00	5.00	5.00	4.00
(a) Without UV	$3.56 \pm 0.22$ (89)	$4.08 \pm 0.31$ (82)	$4.09 \pm 0.05$ (82)	$3.94 \pm 0.15$ (98)
(b) With UV				
One cycle	$3.83 \pm 0.23$ (96)	$4.47 \pm 0.33$ (89)	$4.81 \pm 0.06$ (96)	$3.91 \pm 0.10$ (97)
Two cycles	$4.12 \pm 0.12$ (103)	$4.87 \pm 0.32$ (97)	$5.25 \pm 0.17$ (105)	$3.00 \pm 0.31$ (75)
(c) With UV+H <sub>2</sub> O <sub>2</sub>				
One cycle	$3.81 \pm 0.07$ (95)	$4.92 \pm 0.02$ (98)	$5.05 \pm 0.22$ (101)	$3.57 \pm 0.11$ (89)
Two cycles	$4.10 \pm 0.07$ (102)	$5.10 \pm 0.09$ (102)	$5.00 \pm 0.03$ (100)	$2.67 \pm 0.13$ (67)
<i>SRM 1643d</i>				
Certified values	$6.47 \pm 0.37$	$20.50 \pm 3.80$	$18.15 \pm 0.64$	$1.27 \pm 0.06$
Without UV	$5.97 \pm 0.04$ (92)	$16.36 \pm 0.09$ (80)	$15.17 \pm 0.11$ (84)	$1.17 \pm 0.01$ (92)
With UV (two cycles)	$6.41 \pm 0.02$ (99)	$20.61 \pm 0.25$ (101)	$17.78 \pm 0.11$ (98)	$1.10 \pm 0.01$ (87)

Recoveries in % are given in parenthesis. The errors are given at the 95% confidence level.

and an H<sub>2</sub>O<sub>2</sub> addition was not necessary for these metals. For Cu, two cycles of UV-irradiation and/or H<sub>2</sub>O<sub>2</sub> addition were necessary.

A second set of experiments was carried out on NIST SRM 1643d reference water sample (Table 3). Similar behavior to the UFS solution was observed. Indeed, without UV-irradiation, Cd, Cu and Pb contents appeared lower than expected, whereas they were close to the certified values after two UV cycles.

In both cases the recovery of Ag was almost 100% without any pretreatment, and decreased when UV (with or without H<sub>2</sub>O<sub>2</sub> addition) was applied. Actually, this metal is well known to be highly photo-sensitive,

and some difficulties may occur during the chelating processes, following UV exposure.

These results clearly show that the degradation of OM by UV is effective, and even indispensable, for accurate Cd, Cu and Pb measurements after Chelex-100 resin preconcentration. For both freshwaters used here, two cycles of UV-exposure can be recommended. It is interesting to note that such operating conditions are in agreement with the previous findings derived from fluorescence measurements described above. However, as proved by the first set of experiments, the UV-irradiation time needed to achieve good recovery may be different depending on the element.

In fact, the metals weakly associated with organic complexes (such as Pb and Cd in natural water [23]) are more easily released by UV-irradiation than those strongly complexed (such as Cu [24]). In addition, the UV-exposure time should be adapted for each particular case, depending on the organic matter content. H<sub>2</sub>O<sub>2</sub> does not significantly improve column retention and may be eliminated from the procedure. Ag should not be measured after UV-irradiation.

#### 4. Conclusions

The choice of a method depends on different criteria: the quality of the results desired, the time consumed and the cost of reagents and materials used. The combination of UV-irradiation and Chelex-100 preconcentration should be extensively used for low metal content determinations in natural freshwaters. The technique is cheap and easy to adopt in any laboratory with only a minor increase in the preparation time. It allows a significant improvement of the accuracy of Cd, Cu, and Pb measurements. However, a few preliminary tests should be conducted for each particular kind of water (estuarine and river waters, wastewaters) to determine the UV-irradiation time required for the efficient separation of the metals from the organic ligands.

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