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# Microwave Assisted Micellar Extraction Method Combined with Graphite Furnace Atomic Absorption Spectrometry For The Determination of Ni, Cr, Cu, Pb And Cd in Marine Sediments

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A new green method has been developed for the extraction of the pseudo-total content of the heavy metals Ni, Cu, Cr, Pb, and Cd from marine sediments using a mixture of biodegradable micellar media (SDS, Triton X-100) as extractants and graphite furnace atomic absorption spectrometry (GFAAS) for their determination. This work is the first one that uses only surfactants as extractants, without the addition of chelating agents to increase the extraction efficiency of the method, proving to be effective in the extraction of metals from this type of matrices. The proposed method has shown high recovery percentages for all the metals considered (>68%), good linearity and reproducibility (RSD<5.9%), as well as detection limits ranging from 0.06 to 2.78 µg $g^{-1}$. The method was applied to the determination of the heavy metals under study in samples with different physicochemical properties. Finally, our results were compared with those obtained using microwave assisted extraction - furnace atomic absorption spectrometry (MAE/GFAAS) described in ISO 11047:1998 obtaining comparable results.

## Introduction

The term "heavy metal" is presented as an ill-defined umbrella term for various elements (mainly transition metals, but also some non-metals). Most definitions are based on different physico-chemical properties, specifically in their different densities and their relative atomic mass (between 23-40). As a result, the number of elements that are considered as "heavy metal" varies widely from one author to another (1-4).

Nevertheless, Hübner et al. (5) raise four different options for the use of the term "heavy metal", although they suggest that the term applies to the following elements: arsenic, cadmium, chromium, cobalt, copper, lead, mercury, nickel, tin and zinc. Heavy metals considered in this study (Ni, Cr, Cu, Pb and Cd) are categorized as priority pollutants by the U.S. Environmental Protection Agency (6). They have proved to be important pollutants in the marine environment, with high toxicity, long persistence and rapid accumulation at living organisms (7-9).

Due to the hydrophobic behaviour of these metals, their concentration in seawater is very low, and they instead tend to accumulate in marine sediments (8-12).

This trend is due to adsorption, co-precipitation and metal complexation in the surface layers of fine sediment particles. Thus, four types of metal fractions can be distinguished: (a) the exchangeable fraction, which is located in the ion exchange sites and it is freely available to take part in chemical reactions, (b) the reducible fraction, consisting of complex oxides and hydroxides, which is soluble under reducing conditions, (c) the oxidizable fraction, which is formed with the organic matter and sulphides, and it is available under oxidizing conditions, and (d) the residual fraction, which is introduced into the environment in crystalline form by geological processes and it is generally not available (13).

On the other hand, smaller particles have a higher surface/volume ratio, so they can retain high concentrations of metals, whose distribution and accumulation is also influenced by the sediment grain size, the mineral composition, the oxidation/reduction status, adsorption and desorption processes and physical transport (8).

Then, marine sediments act as metal reservoirs and, for that reason, the analysis of metals in marine sediments allows us to detect pollution in the marine environment and provide information about the ecosystem health (8-11).

Traditionally, methods for extraction and analysis of metals in marine sediments use highly toxic and corrosive extractants; strong acids are often used (14). These extractants have to be applied for long periods (12 hours) and high temperatures (180°C), a process known as "acid digestion". In order to achieve a complete removal of the pseudo total metal content, the exchangeable fraction mentioned above (9), acids as HCl or $HNO_3$ are used; they can remove this fraction of metals avoiding that fraction incorporated into the mineral structure of the sediments joins to silicates, also called residual fraction (15). To remove this residual fraction, which would enable the determination of the total metal content, HF must also be used (16, 17).

This methodology can be combined with the application of microwave energy, a process known as microwave assisted digestion (18, 19), which provides a faster heating alternative, allowing shorter radiation times (usually less than 30 minutes) (20-22). Furthermore, this methodology permits to work simultaneously with multiple samples in a single step, thereby reducing the total time of the procedure (19, 23). Moreover, it requires smaller amounts of extractant (14, 24) and, as compared with other traditional digestion methods, it ensures greater reproducibility (25).

In this sense, a variation of microwave-assisted digestion employs diluted $HNO_3$ solutions for the removal of the pseudo total metal content (26). This method generates fewer residues, leads to lower standard deviations and does not require high dilution factors before analyte measurements. Nevertheless, using of diluted solutions of nitric acid involves generation of NO, $NO_3^-$ and other type of organic residues (26, 27). And, in any case, highly corrosive and toxic acids that should be avoided are still used.

Therefore, a safer and environment-friendly alternative consists in replacing these acids by surfactants which are not toxic, not volatile, and not easily flammable and are also biodegradable (28-30). The use of surfactants as extractants allows adapting the technique of Microwave Assisted Digestion (MAD) to completely avoid the use of toxic and corrosive acids, a method known as Microwave Assisted Micellar Extraction (MAME) (31).

The employment of surfactants as extractants for metals has already been tested in aqueous samples with satisfactory results (32, 33). Surfactants that are generally used for metal extraction are anionic surfactants such as Sodium Dodecyl Sulphate (SDS), which has the ability to extract metals by ionic interaction (32, 34). Non-ionic surfactants are also used, such as Triton X-100 or Triton X-114, due to their hydrophobic interaction with metals (28, 32, 34). Mixtures of these two types of surfactants are also employed due to their synergistic combination, as it has been demonstrated in various studies (28, 34, 35).

However, this kind of studies usually employs chelating agents to ease the extraction. For example, Sang *et al.* (36) used, prior to the aluminium extraction with Triton X-114, the PMPP (1-phenyl-3-methyl-4-benzoyl-5-pyrozolone) as chelating agent. Tang *et al.* (37) used APDC (Ammonium pyrrolidinedithiocarbamate) previously to Arsenic extraction with Triton X-114, and Chen *et al.* (38) used 5-Br-PADAP (2-5-Bromo-2-Pyridylazo-5-diethylamino-phenol) for lead extraction with Triton X-114.

There is only one study, carried out by our team, which shows the feasibility of using surfactant mixtures in the absence of chelating agents for the extraction and determination of the concentration of metals from organic solid samples, namely at the sea plant *Posidonia oceanica* (39). This method has proved its ability to extract heavy metals at such matrices, also providing results comparable to those obtained by acid digestion (ISO 11047:1998) (39).

Therefore the aim of this work is to optimize the methodology MAME for the extraction of the pseudo total content of nickel, chromium, copper, lead and cadmium in marine sediments by using exclusively surfactants (Sodium Dodecyl Sulphate (SDS) and Triton X-100) and its subsequent analysis by Graphite Furnace Atomic Absorption Spectrometry (GFAAS).

## Material and methods

### Reagents

All reagents were provided by PANREAC (Barcelona, Spain). Heavy metal standards (Ni, Cr, Cu, Pb and Cd) were of 1 g $L^{-1}$ ± 0.002 g $L^{-1}$. Stock solutions of each metal were prepared with $HNO_3$ "Hyperpure" at 30 μg $L^{-1}$, except Cd solutions, which were prepared at 3 μg $L^{-1}$, with $HNO_3$ "Hyperpure" 1% ($v\ v^{-1}$) and bi-distilled water.

A standard solution of palladium is used as chemical matrix modifier in metal determination by GFAAS. This modifier is prepared at concentrations of 100 and 500 mg $L^{-1}$ for Cd and Pb, respectively, with $HNO_3$ "Hyperpure" 1% ($v\ v^{-1}$) and bi-distilled water. The anionic surfactant SDS and non-ionic Triton X-100 were prepared in bi-distilled water. The buffers employed, Phosphoric acid/Monopotassium Phosphate, Sodium acetate/Acetic acid Sodium, Monopotassium Phosphate/Dipotassium Phosphate, and Ammonium Chloride/Ammonia, stabilize the pH at 2, 4, 7 and 9 values, respectively. These buffers were also prepared in bi-distilled water.

### Apparatus

The microwave system used to perform the microwave assisted extraction process was a CEM® Xpress chamber (CEM Corporation, Matthews, NC, USA), with a rotor of 16 teflon vessels (CEM Corporation, USA) and term strips Kager GmbH, model A (Kager Industrietechnik, Germany), for the temperature control.

The Atomic Absorption Spectrometer was provided from Agilent Technologies, model AA240Z (Agilent Technologies, USA), with a longitudinal Zeeman Effect background correction system furnished with a Graphite Tube Atomizer GTA 120. Sample solutions were injected into the atomizer by using a programmable sampler dispenser (PSD 120) provided from Agilent Technologies (Agilent Technologies, USA). Graphite Omega Platform Tubes and GTA Tubes Partitioned Pyro-coated were provided from Agilent Technologies Spain, S.L. (Madrid, Spain).

A drying oven provided from Binder, model ED115# 04-69105 (Binder GmbH, Germany), was used to dry the samples by natural convection.

Samples were sieved by a sieve shaker Cisa, model RP-80 (Allegion Ltd., UK). An electrical accurate balance from Ohaus, model PA214C (Ohaus Europe GmbH, Switzerland), was used to prepare all solutions.

### Procedure

**Sample preparation.** Marine sediments from a non-polluted area (Canet d'En Berenguer, Valencia, Spain) were collected with a Van Veen dredge, washed with bi-distilled water, dried during 24 hours at 105º C and homogenized. The fraction smaller than 250 µm was selected.

**Spiking marine sediment samples.** 0.5 g of sample were spiked with the metal mixture (Ni, Cu, Cr, Pb at 15 mg $L^{-1}$ and Cd at 1.5 mg $L^{-1}$), homogenized and stored during 24 hours in order to obtain a dry and homogeneous sample.

**Microwave assisted micellar extraction, MAME.** 0.5 g of spiked marine sediments were transferred to the Teflon digestion vessels. 0.5 g of non-spiked marine sediment samples were also used to produce the blank samples. Then, 5 mL of acetic acid/sodium acetate buffer (pH = 4) and 5 mL of a mixture composed by anionic surfactant SDS, 1.25% ($w\ v^{-1}$) and non-ionic Triton X-100, 0.1% ($v\ v^{-1}$) were added. The vessels were sealed and placed into a microwave chamber during 5 minutes at 800 W. The content of the vessels was then filtered with 10 mL sterile plastic syringes with cellulose acetate filters, to avoid any possible contamination during the filtration process.

**Atomic Absorption Analysis, GFAAS.** 150 µL of the extract obtained after filtration are diluted in $HNO_3$ 1% ($v\ v^{-1}$), then taken to a final volume of 1500 µL and finally analyzed. The heavy metals were analysed under the optimized analytical conditions (Table 1). Hollow cathode lamps were operated with lamp current in the range of 5-10 mA. Argon was used as protective and purge gas.

**ISO 11047:1998 analysis.** The optimized method was compared with the results obtained using an adaptation of the method established by the International Organization for Standardization (ISO 11047:1998) based on MAE for the extraction of metals and GFAAS as determination technique. 0.5 g of spiked marine sediments were transferred to the teflon digestion vessels. Then, 6 mL of pure HCl and 2 mL of $HNO_3$ were added. The vessels were sealed and placed into a microwave chamber in a program based on control of time and temperature, during 30 minutes at 190º C. The content of vessels was then filtered in a vacuum filtration system, and transferred to flask of 100 mL, being the concentration of HCl 21% ($v\ v^{-1}$) and $HNO_3$ 7% ($v\ v^{-1}$).

500 µL of the extracts obtained were diluted in $HNO_3$ 1% ($v\ v^{-1}$) and taken to a final volume of 1500 µL, to be analyzed under the GFAAS optimized conditions (Table 2).

## Results and discussion

### Optimization of GFAAS analysis

Different variables were considered to optimize the analysis of each metal: wavelength of maximum absorbance, furnace temperatures during drying, pyrolysis step (600°C / 1100°C) and during the atomization step (2100°C / 2600°C). The use of platform tubes and the effect of the matrix modifiers and their concentrations have been studied.

Results are shown in Table 1. Some metals such as Pb and Cd are particularly sensitive to chemical interference when analysed by

Atomic Absorption Spectroscopy. These interferences can be minimized by using platform atomization techniques and the appropriate matrix modifiers.

To study the effect of the platform, analyses were performed for each metal with and without platform tubes. The platform tubes gave the best results only in the case of Cd, providing a cleaner analytical signal. When the temperature of the atomizer walls increases quickly, the sample atomization in the platform is retarded because the sample is not directly in contact with the wall. Therefore, atomization occurs in a less changing environment, and thus the reproducibility is improved (39). Under these conditions, the analytic compounds are not vaporized until the furnace wall and gaseous environment have approached to steady-state temperature, which minimizes any chemical interferences (40).

On the other hand, in order to study the effect of modifiers in the analytical signal of selected metals, analyses were performed using two matrix modifiers in $HNO_3$ 1% ($v\ v^{-1}$): Pd modifier at two concentrations (100 mg $L^{-1}$ and 500 mg $L^{-1}$) and $NH_4H_2PO_4$ modifier at 10% ($v\ v^{-1}$). In this case, a cleaner signal was obtained when Pd modifier was used in the case of Cd and Pb at 100 and 500 mg $L^{-1}$ concentrations, respectively. This could be due to the ability of the matrix modifier decreasing the volatility of the analyte or increasing the volatility of a sample matrix component. The element could be prematurely lost in the graphite furnace temperature cycle, but with the addition of the matrix modifier, Cd and Pb can be stabilized at higher temperatures and reduce matrix interferences (41).

### Optimization of Microwave Assisted Micellar Extraction

This work has been performed with real matrices of marine sediments. In order to eliminate the possible noise introduced by the matrix as well as by the initial concentration of metals in the matrix, blank samples were made in all conditions of the variables below.
To the study for the optimization of metal extraction, only SDS is used. Initial experimental conditions were as follows: 5 mL of buffer solution with pH 4, 5 mL of SDS solution 1.25% ($w\ v^{-1}$), power and time radiation of 400W and 5 min, respectively.

**pH effect.** pH is one of the variables that highly affect the adsorption of metals such as Cd, Cu or Pb (42).

The effect of the pH on the metal recovery was determined by analysing the spiked samples with 5 mL of SDS 1.25% ($w\ v^{-1}$) solution as extractant at different pH values. 5 mL of buffer solution with pH 2, 4, 7 and 9 is added in each case. The samples are irradiated in the microwave chamber at 400 W during 5 minutes, then filtered and finally analyzed in GFAAS.

Figure 1 shows that the general trend in the recoveries increases until pH=4; recovery drops for higher pH values. Recoveries are notable in the case of chromium and nickel at pH=4, reaching 90 and 91% respectively. In the case of lead, copper and cadmium, recoveries at pH=4 were 75, 58 and 61% respectively.

This behaviour is probably because for low pH values the anionic SDS micelles are saturated due to the high presence of H+ ions, rendering them ineffective, as shown by some studies (43). On the other hand, metals are retained on inorganic matrices such as soil or sludge for higher pH values (44), because these matrices can retain these metals either by cationic exchange capacity or by their chelating ability (45).

Therefore, pH=4 was taken as the optimum pH value for the following analyses, which corresponds to the buffer solution of acetic acid/sodium acetate.

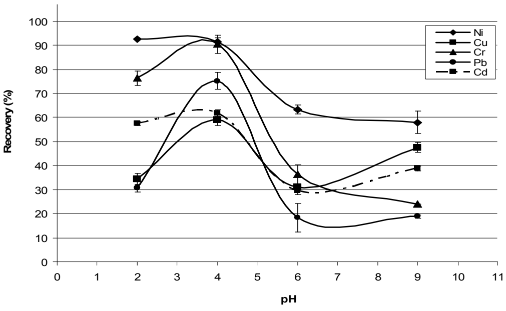

Fig. 1. Effect of pH on the recovery of the metals under study. SDS concentration: 1.25 *($w\ v^{-1}$)*; radiation power: 400W; radiation time: 5 min. (n=3).

**SDS concentration effect.** In order to determine the effect of SDS concentration on the metal recovery percentages, several samples containing different SDS concentration were analyzed. The SDS concentrations considered were 0.25, 1.25, 2 and 2.5% *($w\ v^{-1}$)*, in all cases over Critical Micellar Concentration (CMC) (0.236%, $w\ v^{-1}$). The recoveries obtained are shown in Figure 2.

In this figure, it can be observed that metal recoveries increase slightly until a SDS concentration of around 1.25% in each case; then, recoveries remain rather constant when increasing the SDS concentration. Therefore, SDS concentration optimal value was taken as 1.25% ($w\ v^{-1}$).

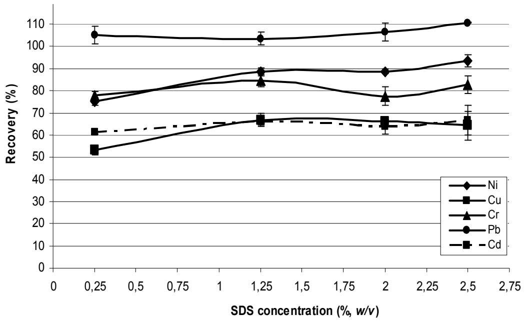

Fig. 2. Effect of SDS concentration on the recovery of the heavy metals. pH: 4; radiation power: 400W; radiation time: 5 min. (n=3).

**Effect of Triton X-100 concentration.** In order to improve the extraction recoveries by the synergistic effect of the SDS with non-ionic surfactants, the effect of Triton X-100 (non-ionic surfactant) is evaluated. For this, several samples containing SDS (1.25%, *w* $v^{-1}$) and Triton X-100 with different concentrations are analyzed. Triton X-100 concentrations considered are 0.1, 0.25, 0.35 and 0.5% *(v* $v^{-1}$*)*, in all cases over CMC (0.0155%, *v* $v^{-1}$). The recoveries obtained are given in Figure 3. The general trend shows that there is no variation in recovery percentages with respect to the concentration of Triton X-100. However, recoveries are greater in the presence of this surfactant in the mixture for Cd and Cu, as compared to Figure 2.

Therefore, the optimal Triton X-100 value was taken as the lowest concentration giving the highest extraction results, 0.1% (*v* $v^{-1}$)

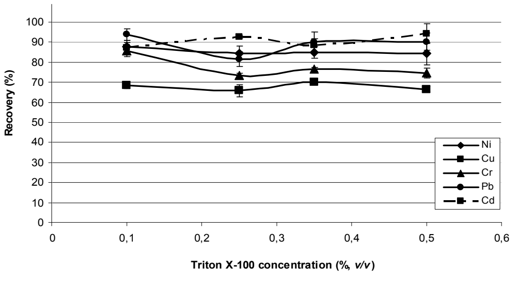

Fig. 3. Effect of Triton X-100 concentration on the recovery of the heavy metals. SDS concentration: 1.25% (*w* $v^{-1}$); pH: 4; radiation power: 400W; radiation time: 5 min. (n=3).

**Effect of the microwave radiation power and time.** Temperature achieved inside the vessels determines the efficiency of the extraction. Since temperature depends on the radiation time and power applied, both variables were analyzed simultaneously. A central composite design was followed in order to study the effect on the recovery. A two-level full factorial design, $3^2$, with a star orthogonal composite design and three central points (11 runs in total) allowed the direct evaluation of the considered variables (46).

Therefore, sediment samples were analyzed using the previously optimized conditions (pH=4, SDS:Triton X-100 (1.25%, *w* $v^{-1}$ :0.1%, *v* $v^{-1}$)) at different microwave powers ranging from 400 to 1600 W, while radiation times does from 2.5 to 10 minutes. Figure 4 shows the recovery percentage surfaces as a function of radiation time and power. Recovery percentages increase with power until 800 W, while it decreases for higher radiation times and power. This may be due to silicides formation, which are binary compounds formed by both transition metals and silicon under high pressure and temperature conditions (47, 48); these compounds may interfere with the metal extraction and their subsequent analysis.

Thus, 2.5 minutes and 800 W were taken as the optimum values for further analyses, which reaches a temperature of 66º C.

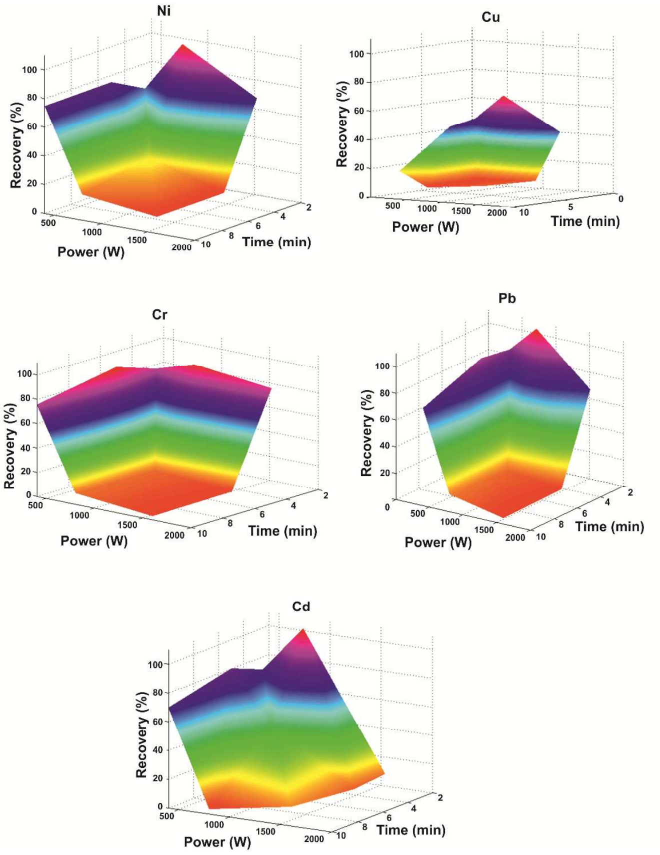

Fig. 4. Effect of the microwave radiation time and power on the recovery of the heavy metals using SDS:Triton X-100, 1.25% (*w v*$^{-1}$) and 0.1% (*v v*$^{-1}$) respectively and pH: 4 (n=3).

**Analytical parameters**

The corresponding calibration curves were obtained by injecting standard solutions containing a known concentration of the metals into the atomic absorption spectrometer system (Table 3). The results revealed a linear relationship with high correlation coefficients (0.999) in the interval 1.5-30.00 µg L$^{-1}$ for all metals except Cd, whose interval is 0.2-3.00 µg L$^{-1}$.

In order to study the reproducibility, the optimized method was applied to the analysis of six samples containing the mixture of metals (Ni, Cu, Cr, Pb at 15 mg L$^{-1}$ and Cd at 1.5 mg L$^{-1}$) which were determined at the established conditions. The relative standard deviation (% RSD) values are listed in Table 3. RDS values obtained are lower than 5.86%. The limits of detection (LOD=$X_b+3\sigma$) and limits of quantification (LOQs) (LOQ=$X_b+10\sigma$) were also calculated once the MAME method was fully applied (Table 3) (49). LOD values obtained for the optimized method are in the range of 0.01 to 0.45 µg g$^{-1}$. These LODs are very similar or even lower than those obtained in other studies using alternative methods (50-52). LOQ values obtained for the optimized method are in each case: 0.35 µg g$^{-1}$ for Ni, 0.53 µg g$^{-1}$ for Cu, 0.45 µg g$^{-1}$ for Cr, 1.49 µg g$^{-1}$ for Pb and 0.04 µg g$^{-1}$ for Cd.

Finally, the results obtained are compared with those obtained using an adaptation of the method established by the International Organization for Standardization (ISO 11047:1998) which consists of MAE as extraction method and GFAAS as determination technique. The recoveries obtained with both methods are comparable (Table 4), and even higher values are obtained in the case of Ni, Cr and Pb with the optimized method. This demonstrates the ability of the proposed method for its application on this type of matrices.

**Analytical applications.**

**Application to different samples of marine sediments**:

The optimized method was applied to two marine sediment samples from presumably uncontaminated environments (a port outside of Pobla de Farnals, Valencia, Spain (M1), and another of El Palmar, Cádiz, Spain (M2)), whose characteristics are shown in Table 5. Specifically, the pH, organic matter content and granulometry are taken into account.

The samples were sieved taking here the fraction < 250 µm. In all cases, 0.5 g of sample were spiked with a mixture of metals with the following concentrations: 3 µg L$^{-1}$ for Ni, Cr, Cu and Pb, and 0.3 µg L$^{-1}$ for Cd. Subsequently, metals were extracted under the optimized method conditions. Nevertheless, in order to eliminate the possible noise introduced by the different matrices as well as by the initial concentration of metals in each matrix, blank samples were made for all the samples studied. The results are shown in Table 6.

The results obtained with the matrix used in optimizing the method (M0) are quite similar to those obtained in the analysis of samples M1 and M2, with the exception of Ni and Cr. This is probably due to the difference in organic matter content, higher in the latter, since differences in particle size and pH of the samples are very small, specially between M0 and M2. This could be explained because the organic matter inhibits the extraction of analytes affecting their solubilization, mobilization and retention due to the strong interaction established between the analyte and the matrix (50), acting as a whole phase, which hinders its rupture (25, 53, 54). From these results, it could be accepted that the method is applicable to real sediment to analyze their content in Cd and Pb. In the case of Ni and Cr, the method could be applied when the organic matter content is below 1%; finally, in the case of Cu, the method would require additional optimization to ensure better removal performance.

**Application of the optimized method to aged samples**: In some studies, it has been shown a variation in the type of chemical bond established between the analytes and the matrix over time (53). Initially the analytes are incorporated only by surface adsorption, where the formation of hydrogen bonds and interactions by Van der Waals forces are the dominant processes. Subsequently, the analytes are strongly bound to the organic matter due to diffusive transport mechanisms and sequestration that involves sorption at remote microsites within the matrix (53). Thus, recovery percentages are also affected by the aging effect of the samples (32, 53, 55-57).

This issue is addressed here by enriching the matrix and leaving it in contact with the analytes during 4 months. Later on, extraction and analysis are performed under the optimized conditions. The results are shown in Table 7. Cd shows high recovery percentages, but for the remaining metals, recovery percentages obtained for the aged samples are lower than those obtained with the optimized method applied to recent spiked samples (55 and 93%). This confirms a well known phenomenon (32, 53, 56, 57) also shown in other extraction techniques (53) that can be explained by the type of interaction that occurs over time. In this sense, the results are similar to those expected, although for the application of the proposed method new conditions of extraction should be used.

## Conclusions

This study proves for the first time the suitability of the mixtures of anionic and non-ionic surfactants as extractants for heavy metals from marine sediments in the absence of any chelating agent.

The proposed method seems to be an adequate alternative for the extraction of heavy metals at this type of matrices because of all these advantages: it does not require deep handling and the extract can be analyzed without requiring a complicated intermediate treatment; combining surfactants as extractants with the microwave assisted extraction enhances method skills because extraction is faster and less extractant is needed; it can be applied to the extraction of several samples at the same time without toxic effects. On the other hand, the method drops off the costs dramatically and it is relatively straightforward.

It has also shown to provide good results comparable to those obtained with the official method. Therefore, this promising method could be an alternative to extract heavy metals from marine sediments and it could be applied as a routine analysis for the determination of Cd and Pb. The application of the proposed method to the analysis of Ni, Cu and Cr in aged samples, would require new extraction conditions.

## Notes and references

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TABLES

Table 1. Conditions for the determination of Cd, Cr, Cu, Ni and Pb using GF AAS.

| **Analyte** | **λ (nm)** | **Temperature Ramp** | | **Matrix modifier** | **Graphite tube** |
|---|---|---|---|---|---|
| | | **Drying and Pyrolysis step** | **Atomization step** | | |
| Ni | 232.0 | 1100º C / 17 s | 2500º C / 5 s | No | No platform |
| Cu | 327.4 | 900º C / 8 s | 2300º C / 5 s | No | No platform |
| Cr | 357.9 | 1100º C / 12 s | 2600º C / 5 s | No | No platform |
| Pb | 283.3 | 600º C / 17 s | 2100º C / 3 s | Pd 500 ppm | No platform |
| Cd | 228.8 | 700º C / 22 s | 2100º C / 5 s | Pd 100 ppm | Platform |

Table 2. Conditions for the determination of Cd, Cr, Cu, Ni and Pb using ISO 11047:1998 method.

| **Analyte** | **λ (nm)** | **Temperature Ramp** | | **Matrix modifier** | **Graphite tube** |
|---|---|---|---|---|---|
| | | **Drying and Pyrolysis step** | **Atomization step** | | |
| Ni | 232.0 | 900º C / 8 s | 2650º C / 5 s | No | No platform |
| Cu | 327.4 | 800º C / 17s | 2300º C / 3 s | No | No platform |
| Cr | 357.9 | 1000º C / 13 s | 2600º C / 5 s | No | No platform |
| Pb | 283.3 | 400º C / 20 s | 2200º C / 3 s | Pd 500 ppm | Platform |
| Cd | 228.8 | 500º C / 19 s | 1800º C/ 5 s | Pd 500 ppm | No Platform |

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Table 3. Analytical parameters of the optimized method.

| Analyte | RSD (%) [a] | LOD (μg $g^{-1}$)[b] | LOQ (μg $g^{-1}$)[b] | $\gamma^{c}$ | Linear Range (μg $L^{-1}$) |
|---|---|---|---|---|---|
| Ni | 3.01 | 0.10 | 0.35 | 0.0011 | 1.5 - 30.00 |
| Cu | 5.75 | 0.21 | 0.53 | 0.0006 | 2.5 - 30.00 |
| Cr | 2.78 | 0.13 | 0.45 | 0.0046 | 2.5 - 30.00 |
| Pb | 5.86 | 0.45 | 1.49 | 0.0003 | 7.5 - 30.00 |
| Cd | 2.43 | 0.01 | 0.04 | 0.0239 | 0.2 - 3.00 |

[a](n=6); [b](n=10); [c]Analytical Sensitivity

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Table 4. Comparison of the optimized method and ISO 11047:1998 method to the analysis of marine sediment (n=3).

| **Analyte** | **Amount added (μg $g^{-1}$)** | **Results by MAME-GFAAS (μg $g^{-1}$)** | **Results by ISO 11047:1998 (μg $g^{-1}$)** |
|---|---|---|---|
| Ni | 3.00 | 2.69 ± 0.09 | 2.55 ± 0.71 |
| Cu | 3.00 | 2.06 ± 0.17 | 2.26 ± 0.18 |
| Cr | 3.00 | 2.77 ± 0.08 | 2.50 ± 0.12 |
| Pb | 3.00 | 3.11 ± 0.18 | 2.50 ± 0.12 |
| Cd | 0.30 | 0.31 ± 0.07 | 0.31 ± 0.05 |

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Table 5. Physico-chemical properties of marine real samples. M0: Sediment of the optimized method, M1: Pobla Farnals beach (Valencia, Spain), M2: El Palmar Vejer (Cadiz, Spain).

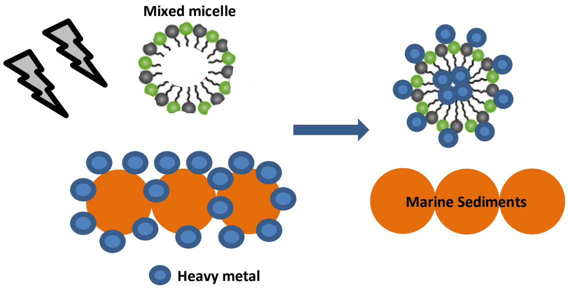
| **Physico-chemical properties** | **M0** | **M1** | **M2** |
|---|---|---|---|
| Organic Matter (%) | 0.75 | 2.08 | 1.23 |
| Ø>2mm (%) | 0.12 | 4.97 | 0.10 |
| 63µm<Ø<2mm (%) | 99.88 | 86.85 | 99.90 |
| Ø<63µm (%) | 0.00 | 8.18 | 0.00 |
| pH | 8.47 | 8.02 | 8.37 |

Table 6. Application of the optimized method to marine real samples. M0: Sediment of the optimized method, M1: Pobla Farnals beach (Valencia, Spain), M2: El Palmar Vejer (Cadiz, Spain) (n=3). Amount added: 3.00 µg g$^{-1}$ for Ni, Cu, Cr and Pd; and 0.3 µg g$^{-1}$ for Cd.

| **Analyte** | **M0**<br>**Recovery (%)** | **M1**<br>**Recovery (%)** | **M2**<br>**Recovery (%)** |
|---|---|---|---|
| Ni | 89.63 ± 3.01 | 73.74 ± 2.35 | 75.07 ± 2.55 |
| Cu | 68.60 ± 5.75 | 61.07 ± 0.10 | 56.80 ± 5.19 |
| Cr | 92.40 ± 2.78 | 71.03 ± 4.10 | 73.35 ± 2.06 |
| Pb | 106.77 ± 5.86 | 101.93 ± 9.93 | 111.53 ± 8.01 |
| Cd | 106.33 ±2.43 | 105.33 ± 9.41 | 104.45 ± 9.10 |

Table 7. Comparison between metal recovery percentages for aged and recent marine sediment samples (n=3). Amount added: 3.00 µg g$^{-1}$ for Ni, Cu, Cr and Pd; and 0.3 µg g$^{-1}$ for Cd.

| **Analyte** | **Recovery (%)** | |
|---|---|---|
| | **recent marine sediments** | **aged marine sediments** |
| Ni | 89.63 ± 3.01 | 63.97 ± 0.62 |
| Cu | 68.60 ± 5.75 | 57.80 ± 0.42 |
| Cr | 92.40 ± 2.78 | 55.49 ± 0.83 |
| Pb | 106.77 ± 5.86 | 79.29 ± 3.29 |
| Cd | 106.33 ±2.43 | 93.78 ± 0.83 |


Mixed micelle
Marine Sediments
Heavy metal