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Simple and low cost dithizone-functionalized polymer membranes as a tool for mercury preconcentration and monitoring in aqueous bodies. Preliminary results using X-ray absorption near-edge structure (XANES)

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Abstract

Here the effectiveness of cation selective membranes, produced for divalent mercury (Hg^{2+}) preconcetration from aqueous bodies, is examined. To this end, the behavior of PVC-based membranes, functionalized with dithizone for mercury complexation, is examined by means of Energy Dispersive X-ray Fluorescence (EDXRF) and total reflection - X-ray absorption near-edge structure (TXRF–XANES) techniques. In our previous works, we successfully immobilized dithizone on PVC-based thin film substrates, creating novel Hg-selective membranes, and identified the optimal experimental parameters affecting mercury sorption from water samples. Nonetheless, the question remains, to what extent dithizone is responsible for mercury complexation on the membrane surface, or it just improves the membrane's active surface area thus simply improving the adsorptive effect. Using the EDXRF technique it appears that membranes functionalized with dithizone has a much higher efficiency (by up to threefold) in preconcetrating mercury from water matrices, compared to the non-functionalized membranes. Then, the membranes were also examined by means of TXRF–XANES and it was identified that indeed mercury-dithizone complex is produced on the membrane surface, which is responsible for the much higher mercury sorption, compared to the non-functionalized membranes. Also, the XANES mercury-dithizone spectrum is presented. Given polymer membrane simple manufacturing procedure and their low cost this study works towards establishing a new method for very low concentration mercury analysis (sub-ppb levels) as well as mercury collection from aqueous bodies, provided that the membranes are produced and used in large-scale routine works.

Keywords: Mercury (Hg), dithizone ($C_{13}H_{12}N_4S$), polymer membranes, water matrices, heavy metal pollution.

1. Introduction

Mercury is considered a major environmental pollutant and one of the most toxic elements that may be found in aqueous bodies, since exposure to miniscule concentration (ppb) can cause detrimental health effects (Elias *et al.*, 2018; Kallithrakas-Kontos and Foteinis, 2016). It is a persistent and highly toxic heavy metal, which can cause severe biological toxicity on the nervous, digestive, and immune system, among others (Kallithrakas-Kontos and Foteinis, 2016).

Mercury occurs naturally (e.g. volcanic activity and weathering of rocks), but most of the mercury in the environment result from human activities; particularly from coal-fired power stations -the main source of mercury found in the atmosphere-, artisanal gold mining (where mercury is used to form an amalgam before being burnt off), landfilling, and dental materials (Riccardi *et al.*, 2013; WHO, 2007). For example, only in the United States (US) around 44 tons of mercury are emitted annually from coal-fired power plants, accounting for more than 30% of emissions from all anthropogenic mercury sources (Liu *et al.*, 2016).

Mercury largely occurs in its elemental (Hg(0) - a liquid or monatomic vapour), or its oxidized (Hg^{2+} - divalent mercury or mercuric ion) form, with both undergoing redox changes in biotic and abiotic processes (Riccardi *et al.*, 2013). Redox cycling between Hg(0) and Hg^{2+}, which is driven by both photochemical processes and dark reactions, is the key mechanism for mercury transport in groundwater systems (Colombo *et al.*, 2014). Furthermore, Hg^{2+} is the substrate for the production of neurotoxic methylmercury, which enters food webs and biomagnifies at higher trophic levels (Colombo *et al.*, 2014). Therefore, even though Hg(0) is relatively unreactive, when oxidized to Hg^{2+} it becomes highly reactive, neurotoxic, nephrotoxic, hepatotoxic, and immunotoxic (Riccardi *et al.*, 2013).

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As a result, mercury is classified a "Priority pollutant" in the EU (2000/60/EC), with an established limit for drinking water as low as 1 μg L^{-1} Hg (Elias *et al.*, 2018; Marguí *et al.*, 2018). Furthermore, the World Health Organization (WHO) has recommended the reduction or elimination of releases of mercury and its compounds to the environment (WHO, 2007). Even though due to legislation initiatives mercury's industrial usage has been reduced (Hatzistavros and Kallithrakas-Kontos, 2014), the facts that: a) mercury has been used by humans for more than 3 500 years (Kallithrakas-Kontos and Foteinis, 2016), and b) existing anthropogenic sources will continue to emit thousands of metric tonnes of mercury into the environment, adding to the naturally releases (e.g.volcanoes and deep sea vents) (Riccardi *et al.*, 2013), are indicative of the extent of the problem. Thus, it is clear that mercury monitoring, assessment, and, most importantly, collection from natural water bodies remains imperative to protect human health and the environment.

Given mercury's high toxicity, various methods and technologies for its collection from the environment, such as phytoremediation, bioremediation, activated carbon adsorption, and extraction, have been proposed (Atwood and Zaman, 2006). The use of adsorptive matrices for mercury capture from aqueous streams has been extensively reported in literature, focusing on various thiol-functionalized materials like resins, particles, or composite materials as mercury ion capture modalities (Smuleac *et al.*, 2005). Moreover, the use of chemical reagents, particularly thiol-based ligands, for mercury removal from aqueous systems have been proven effective in precipitating mercury (Atwood and Zaman, 2006). The reason is that, from the principles of hard–soft acid–base chemistry, mercury has a very strong affinity towards sulphur (Smuleac *et al.*, 2005). Hence, Hg^{2+} is most frequently bonded to deprotonated thiol donors in natural organic matter and biological systems (Manceau *et al.*, 2015).

Among the many thiol-based ligands that have been examined in the literature, e.g. see (Atwood and Zaman, 2006), dithizone is a well-established and -known ligand (e.g. see (Elly, 1973; Litman *et al.*, 1977). In our previous work (Hatzistavros and Kallithrakas-Kontos, 2014), we created novel Hg-selective PVC-based thin film membranes and identified dithizone as a very promising ligand for mercury preconcentration on environmental water matrices, at trace (ppb) levels.

Here, we assess the effectiveness of the produced Hg^{2+} selective membranes, functionalized with dithizone, on mercury preconcentration/collection. To this end, we produced two types of membranes, one functionalized with dithizone and one without, and used them to collect mercury (25 ng mL−1) from water matrices. Measurements were carried out using EDXRF and XANES techniques. Furthermore, based on the preliminary results we discuss the possibility of the produced Hg^{2+} selective membranes to act as a low cost method for mercury monitoring in natural water bodies, and even mercury collection, should they being produced and employed at large scale.

2. Materials and methods

2.1. Chemical reagents and solvents

For membrane and solvent preparation the following, high quality, analytical reagents were used. For the membrane matrix high molecular weight polyvinyl chloride, i.e. PVC, was sourced from Fluka™ (No. 81387). The membrane solution was prepared using: as plasticizer dibutyl phthalate (DBP) sourced from Riedel-de Haën (No. 36736, Pestanal®); as ionophore, which is used to enhance anion binding on the membrane, 5,5-dithiobis(2-nitrobenzoic acid) (DTNB) sourced from Fluka™ (No. 43760, Ellman's reagent); and as the complexing reagent (ligand) dithizone, sourced from Sigma–Aldrich® (No. 43820).

For the solvents preparation ultrapure water (ASTM Type I) was used, where the dithizone and mercury (Fluka Mercury Standard for Atomic Absorption Spectroscopy AAS (1000±4 mg L−1, Cat. No. 16482) were mixed. The above chemical reagents were in solid form and hence tetrahydrofuran (THF), sourced from Sigma–Aldrich® (No. 401757), was used for their dilution. Finally, as mentioned above, typical ultrapure water (ASTM Type I) was used throughout the work.

2.2. Membrane and solvent preparation

Membranes were prepared directly on thin films (Mylar® 2.5 μm), placed in cylindrical XRF sample plastic cups (Chemplex Cat. No. 1540) at the Analytical and Environmental Chemistry Laboratory, Technical University of Crete, Greece. Specifically, the Membrane solution was prepared by mixing the solvent (PVC matrix) with the plasticizer (dibutylphthalate), the complexing reagent, i.e. ligand (dithizone), and ionophore (DTNB). An in depth analysis and discussion on selective membrane preparation procedure can be found in our previous work (Hatzistavros and Kallithrakas-Kontos, 2014).

In total the performance of two membranes was examined herein. One prepared under the optimal conditions identified by (Hatzistavros and Kallithrakas-Kontos, 2014), i.e. Mylar® 2.5 μm was used as the thin film substrate and the membrane composition (w/w) was 52% PVC, 32% dibutyl phthalate, 9.5% dithizone and 6.5% ionophore, all diluted in THF solvent, and one prepared using the above mixture but without the ligand (dithizone). The latter membrane was prepared to identify the effect the complexing reagent, in this case dithizone, on the membrane efficiency and whether mercury ions would bind on cation selective membrane regardless the ligand. Once the membranes were prepared they were immersed, for 16 h, on a large laboratory flask, containing 1000 mL ultrapure water and 25 ng of mercury. The sample was stirred to enhance the mobility of the mercury ions. After Hg selective collection procedure both membranes were rinsed with high purity water and they were kept for analysis.

For the TXRF-XANES analyses instead of the Mylar® 2.5 µm film, the membranes were immobilization on quartz reflectors. Specifically, the membrane solution was placed on the center of the quartz glass, producing a 10-mm diameter spot and was left to dry at room temperature (a detailed discussion of this procedure can be found in (Koulouridakis and Kallithrakas-Kontos, 2004)). Once the reflectors with each membrane, one with and one without dithizone, were dried they were immersed in the large laboratory flask (25 ng L^{-1} mercury). Also, in order to produce the XANES reference spectra for divalent mercury and for Hg^{2+} -dithizone two solvents were prepared. The first one by diluting 25 ng of mercury in 1000 mL ultrapure water (ASTM Type I), while in the second one apart from the 25 ng of mercury also dithizone was added. Each solvent was stirred to allow the uniform distribution of its content. Then, 10 µL were taken from each solvent and placed on a TXRF quartz reflector and it was left to dry (without heating).

2.3. Apparatus

Sample analyses were performed by means of an Energy Dispersive X-ray fluorescence (EDXRF) unit, to identify the Hg^{2+} content which is also crucial for the XANES measurements, and also by means of X-ray Absorption Near Edge Structure Spectroscopy (XANES) to identify if a mercury-dithizone complex is produced on the membrane surface.

2.3.1. Energy dispersive X-ray (EDXRF) analyses

X-ray fluorescence (XRF) analysis is considered a rather simple analytical technique, in terms of its application and interpretation, offering qualitative and quantitative elemental information at trace level (Karydas *et al.*, 2018). Here we used the Energy Dispersive X-ray Fluorescence (EDXRF) technique to estimate the Hg^{2+} concentration, at sub-ppb levels. Samples were measured by means of an AMETEK® SPECTRO XEPOS unit, a widely used EDXRF spectrometer for environmental monitoring and assessment applications (Kallithrakas-Kontos *et al.*, 2016). The unit has a 12-position autosampler and excitation is achieved through an air-cooled Palladium (Pd) anode X-ray end window tube, with maximum power and voltage 50 W and 50 kV, respectively (Hatzistavros and Kallithrakas-Kontos, 2014). Furthermore, the unit has three excitation modes, the Compton secondary/molybdenum, the Barkla Scatter/aluminum oxide, and the Bragg crystal/highly oriented pyrolytic graphite (HOPG). The unit operated with a silicon drift detector (SDD), with Peltier cooling (i.e. it operates at −25 ◦C without the need for liquid nitrogen input) and an 8 µm Moxtek Dura-Be window. Finally, the peak to background ratio is 5000 : 1 and the detector resolution is 160 eV at 5.9 keV (Foteinis *et al.*, 2013).

Here the Hg^{2+} measurements were performed using the Compton secondary/molybdenum mode at 40 kV and 0.9 mA. Measurements were performed using helium gas flushing, instead of in air atmosphere. Each sample was irradiated for 5 min (300 s). After irradiation, the raw data were processed using X-Lab Pro 4.0 quantitation software and TurboQuant screening method. Hg^{2+} quantification was vital, not only to estimate the efficiency of each membrane in mercury sorption, but also and for XANES measurements, since the mercury content will determine the XANES irradiation time, among others.

2.3.2. X-ray absorption near edge structure spectroscopy (XANES) analysis

The effectiveness of the ligand under study, i.e. dithizone, was assessed by investigating the near-edge part of the absorption spectrum in the tender (X-ray absorption near-edge structure, XANES). In contrast to EDXRF, which can estimate the elemental composition down to the ng/g, XANES offers distinction of chemical forms selected/detected elements, i.e. speciation (Wrobel *et al.*, 2016), in this case Hg^{2+} and Hg^{2+}-dithizone complex. In general, XANES possesses a good chemical-state and ligand sensitivity, because of participation of unoccupied valence orbitals in the excited state and is also sensitive to distant atoms at low kinetic energy of the emitted photoelectron (Manceau *et al.*, 2015). Furthermore, XANES reaches optimum sensitivity when the excitation geometry are carefully adjusted to maximize the fluorescence signal of the analyte element and to reduce spectral background (Wrobel *et al.*, 2016). Nonetheless, the main hurdles for XANES measurements in identifying Hg-binding environments include a) poor spectral resolution due to the large Hg core−hole lifetime broadening (up to 5.5 eV at the L3-edge), which severely degrades chemical-state and ligand sensitivity; and b) the high difficulty to interpret XANES spectra in quantitative molecular structural terms (Manceau *et al.*, 2015).

In this work, XANES measurements were performed at Elettra Sincrotrone Trieste (IAEA End-station). Specifically, the International Atomic Energy Agency (IAEA) through its program activities promotes and supports interdisciplinary research at synchrotron radiation facilities, including the Elettra Sincrotrone Trieste (EST), in Italy (Karydas *et al.*, 2018). In particular, the Physics Section of the IAEA has developed and installed an experimental X-Ray Spectrometry facility, as end-station at the XRF beamline of EST, using 40% of the beam time. The beam is accessible to IEA end-users, such as this case, allowing the synergistic application of various variants of XRF techniques, including XANES (IAEA, 2018).

The ligand environment of the membranes used for the selective absorption of Hg^{2+} was studied by means of Hg-L3 XANES analysis (Hg-L3 edge at 12,284 eV, using the 20-BM-B beamline (sector 20)). The XANES data obtained from the Elettra Sincrotrone Trieste (Figure 1) were processed by ATHENA tool, typically used for XANES data processing (Wrobel *et al.*, 2016). The X-ray fluorescence beamline of the Elettra Sincrotrone Trieste is based on a Si(111) double crystal monochromator (resolving power of 1.4×10^{-4}, photon flux of 108 – 109 s^{-1} in the energy range between 3.65 and 14.5 keV). Moreover, IAES's advanced X-ray spectrometry instrument is equipped with a multi-axis motorized sample manipulator (four linear and three rotational stages that provides different degrees of freedom to align the sample surface relative to the incident beam); an ultra-thin window (UTW) silicon drift detector (SDD, Bruker Nano GmbH, XFlash 5030, 30 mm^2 nominal crystal area, 450 μm crystal thickness and 131 eV energy resolution at Mn-Kα) (Shaltout *et al.*, 2018). As mentioned above, using the XANES spectra it is possible to identify the chemical speciation of trace elements on the sample surface (Karydas *et al.*, 2018), i.e. on the TXRF quartz reflectors.

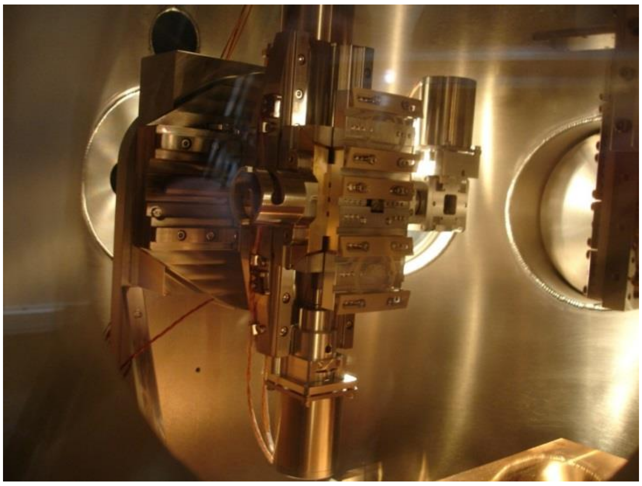

Figure 1. The quartz reflectors with the samples on their surfaces, at TXRF geometry inside the vacuum chamber for XANES measurements at the Elettra Sincrotrone Trieste, Italy

3. Results and discussion

3.1. EDXRF results

In our previous studies, PVC-based, cation selective membranes functionalized dithizone phthalate have been identified as an excellent preconcentration method for mercury analysis in water matrices, using the TXRF or the EDXRF technique (e.g. see (Hatzistavros and Kallithrakas-Kontos, 2014; Koulouridakis and Kallithrakas-Kontos, 2004; Marguí *et al.*, 2018). Here, we applied EDXRF technique to identify the effectiveness of the ligand, i.e. dithizone, on the proposed polymer membranes. Figure 2 shows EDXRF results for polymer membranes funtionalized with the selected ligand and a blank sample.

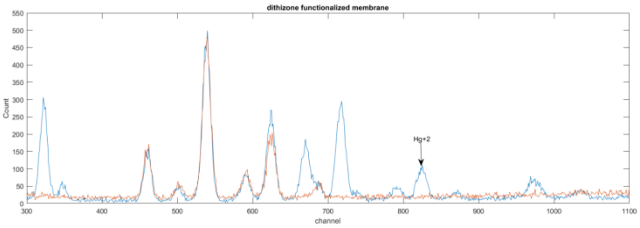

Figure 2. EDXR results for the PVC-based membrane functionalized with dithizone (blue colour) and a blank sample (orange colour)

As far as the efficiency in mercury sorption is concerned, it was found that the dithizone-functionalized membrane exhibited a much higher (up to threefold) efficiency in preconcentrating mercury (data not sown). This is in agreement with the results obtained from our previous work using TXRF (Koulouridakis and Kallithrakas-Kontos, 2004).

This suggest that the presence of a ligand, in this case dithizone a well-known mercury absorbent from water matrices, has a profound effect for mercury preconcertation. Results are also indicative of the many available possibilities of the produced PVC-based polymer membranes, which if applied at large-scale can offer a reliable, sensitive, rapid and most probably economic method, not only for mercury preconcetration, monitoring and assessment, but also for mercury removal from natural water bodies provided that they are used in large-scale routine works.

Even so, results are suggestive of the superiority of the membrane that is functionalized with dithizone, EDXRF cannot shed light if, and to what extent, a mercury-dithizone complex is produced. For this reason the XANES technique was applied, as shown below.

3.2. XANES results

In Figure 3 the XANES spectra of the two membranes, i.e. with and without the ligand (dithizone), as well as the XANES spectra for Hg^{2+} and Hg^{2+}-dithizone complex are shown. The reference XANES spectra for Hg^{2+} and Hg^{2+}-dithizone complexo were obtained by measuring the absorption of the model compounds (i.e. the reference solutions that were placed on TXRF quartz glasses). The Hg^{2+} XANES reference spectra appears to have an intense pre-edge peak, i.e. the energy position of the first peak (E1), an indicator of Hg oxidation, at about 12284.5 eV, which is consistent with the literature (Colombo *et al.*, 2014). The Hg^{2+}-dithizone complex XANES reference spectra appears to have an E1 at 1290 e. As far as the dithizone-functionalized membrane is concerned it exhibited an E1 of 1289.5 eV, very similar to the Hg^{2+}-dithizone complex XANES reference spectra. On the other hand, the non-fuctionalized membrane intense pre-edge peak is not very clear, but it appears to match the Hg^{2+} XANES reference spectra. It has to be noted that the membranes XANES spectra had an overall low quality, especially those the non-functionalized membrane, which is attributed to the very low concentrations of Hg^{2+} on their surfaces. This was expected, since main target of the produced membranes is mercury preconcertation and not collection, while the non functionalized membrane had a much lower efficiency in mercury sorption, which is clearly reflected in the XANES spectra low quality.

Overall, results are suggestive of the non-fuctionalized membrane had indeed adsorbed Hg^{2+}, but at a very low concertation as identified by the EDXRF technique, which is depicted in the XANES spectra low quality. On the other hand, the XANES spectra quality of the dithizone-functionalized membrane was much better, since it the mercury sorption was much higher, but most importantly the spectra fitted the XANES spectra of the reference Hg^{2+}-dithizone complex. Therefore, it is shown that mercury is complexed on the membrane surface due to the presence of dithizone, and not that dithizone just improved the membrane's surface area thus simply improving mercury's adsorptive effect.

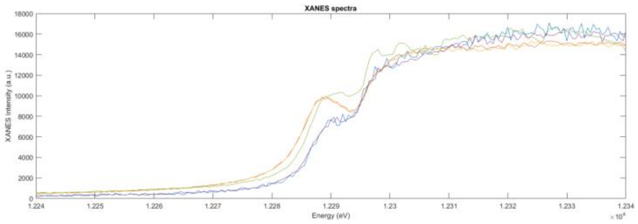

Figure 3. TXRF–XANES spectra of Hg^{2+} (red and orange) and Hg^{2+}-dithizone complex (purple) references along with the XANES spectra of dithizone-functionalized membrane (blue) and the non-functionalized membrane (green)

Given the polymer membrane simple manufacturing procedure, they can be produced without the need of specialized equipment of personnel, and their overall low cost, the chemical reagents required are easy to find and not expensive given the intended purpose, the many possibilities of the cation selective membranes emerge. Specifically, the membranes can be effectively used for mercury preconcetration from natural water matrices, such as seawater. This is imperative since heavy metals pollution in seawater has been extensively reported (Chatzisymeon, 2016)) and given mercury's high toxicity at miniscule concetration (ng L^{-1}), its effective monitoring and assessment remains a difficult task. Furthermore, another possibility that could be addressed in future works is the use of the dithizone-functionalized polymer membranes for large-scale mercury collection from natural waterbodies as well as from industrial waterborne and possibly from airborne emissions, such as from coal-fired power stations emissions, provided that the membranes are produced and used in large-scale routine works.

4. Conclusions

This study worked towards establishing a new method for very low concentration mercury analysis (sub-ppb levels), by examining the mercury species and the complexes that are formed in PVC-based Hg^{2+}-selective membranes, futionalized with dithizone. Using the EDXRF technique it was found that the dithizone-functionalized membrane efficiency in mercury sorption is up to threefold higher, compared to non-functionalized membranes. This is in agreement with results obtained from our previous work using TXRF. In order to identify if mercury is complexed with dithizone on the membrane surface or if dithizone just improves the membrane's active surface area thus simply improving mercury's adsorptive effect the XANES technique was applied. Furthermore, the XANES mercury-dithizone spectrum is given.

It was found that mercury complexes with dithizone directly on the membranes surface, thus substantially improving the membrane's efficiency in preconcentrating mercury from natural water matrices. Also, Then, the membranes were also examined by means of and it was identified that indeed mercury-dithizone complex is produced on the membrane surface, which is responsible for the much higher mercury sorption, compared to the non-functionalized membranes. Given the simple manufacturing procedure, even by non-specialized personnel, and their overall low cost the polymer membranes are excellent tool for mercury preconcetration at trace level (ng L^{-1}) and subsequently for their use as a robust tool for monitoring and assessment application in natural water bodies. Future applications could also include the large-scale mercury collection not only from natural waterbodies, but also from industrial waterborne and possibly from airborne emissions, such as from coal-fired power stations emissions, provided that the membranes are produced and used in large-scale routine works.

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