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## Accepted Manuscript

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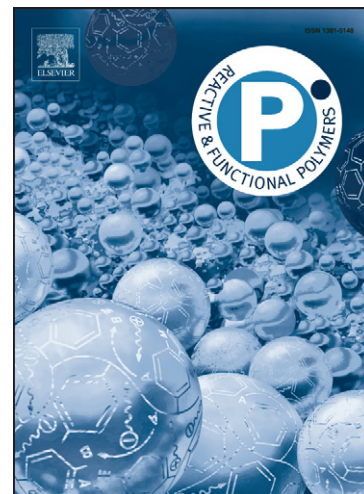
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# Synthesis and applications of XAD-4-DAN chelate resin for the separation and determination of Se(IV)

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## Abstract:

Solid-phase extraction for cationic elements is a promising approach for water treatment or for analysis applications. However, supports that allow the selective extraction and/or preconcentration of metalloid species are still not widespread. A new chelating sorbent has been prepared by grafting 2,3-diaminonaphtalene (DAN) on Amberlite<sup>®</sup> XAD-4 resin beads via a diazo bridge. The synthesis was first carried out at a molecular level to optimize experimental conditions and to facilitate characterization of solid sorbent by FTIR. TGA, Py-GC/MS experiments and back titration of amine functions showed that the sorbent was grafted. Se(IV) was retained by grafted Amberlite<sup>®</sup> XAD-4 with a rate of 88% at pH 2 and 80

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°C. This paper presents a convenient way of grafting DAN on polystyrene-like resins and the first applications of these supports in solid phase extraction of Se(IV).

**Keywords:** poly(styrene-*co*-divinylbenzene) sorbents, grafting, 2,3-diaminonaphthalene, selenite

## 1. Introduction

Grafting specific ligands on synthetic organic sorbents has attracted a great attention for metal uptake, both for analytical purposes [1-6] and for the treatment of raw water [7-12]. Resins based on styrene-divinylbenzene copolymers have often been chosen because of their high surface areas, high mechanical and thermal stabilities and their porosities make them ideal matrices for preparing functionalized supports [13-16]. Among them, Amberlite<sup>®</sup> resin beads made of poly(styrene-*co*-divinylbenzene) (PS-DVB) from the XAD series have often been used for the determination of metallic ions either by the adsorption of the metal complex on the resin followed by its elution and detection [17-19], or by the specific retention of targeted metals onto grafted [20-22] or impregnated resin [23-25]. However, if used as chemosensors or for direct spectrometric determination, the grafting step of the specific ligand is imperative. With this aim, our research group previously grafted Amberlite<sup>®</sup> XAD-4 resin beads with salicylic acid and derivatives for the extraction and/or preconcentration of metallic cations in water [22, 26] and a on-line analyzer has been able to be developed [27].

While various ligands have been grafted on different supports for the extraction/preconcentration of heavy metals, little has been done for the selective extraction of metalloids species. Among these species, selenium has attracted interest because it is an essential nutrient to humans in a limited range of daily intake, but will turn into a toxin at higher levels [28]. Epidemiological studies show that mortality from cardiovascular diseases and cancer might increase as the serum Se level decreases [29]; however, selenium poisoning

may occur if the average intake of selenium is greater than 500  $\mu\text{g/d}$  [30]. Selenium can exist in the environment as Se(0), Se(-II), Se(IV) and Se(VI). Selenite ( $\text{SeO}_3^{2-}$ ) and selenate ( $\text{SeO}_4^{2-}$ ) are the most common species in the aquatic environment [31], and because their level in the environment (10–3800 ng/L in lakes, 16–290 ng/L in rivers, 50–27000 ng/L in groundwaters) [32, 33] is relatively low compared to levels of other ionic species, a procedure allowing their selective extraction/preconcentration could be very useful.

The general methods for the separation and preconcentration of inorganic selenium are based on combining a very efficient separation technique with a sensitive detection technique. Various detection techniques, such as atomic fluorescence spectrometry (AFS) [34], atomic absorption spectrometry (AAS) [35], stripping voltammetry [36], inductively coupled plasma optical emission spectrometry (ICP-OES) [37] and inductively coupled plasma-mass spectrometry (ICP-MS) [38] have been applied to accurately determine trace selenium and its species in various samples. However, direct application of spectroscopic methods for the determination of trace elements in environmental and biological systems is limited due to sample matrix or spectral interferences. Hence, an effective separation method is often required [34-40]. For a simple elemental speciation, especially for different oxidation state of a given element, non-chromatographic methods are more widespread than the chromatographic techniques. Among these non-chromatographic techniques, solid-phase extraction (SPE) has been used due to some merits including convenience, low cost, time saving, reduced solvent utilization, possible miniaturization and easy automation [27].

In this paper, we propose the grafting of 2,3-diaminonaphthalene (DAN) via a diazo spacer on Amberlite<sup>®</sup> XAD-4 resin beads. DAN is a commonly used reagent for selenium determination : Se(IV) reacts in organic solvents with DAN to form the complex piarselenol [41]. This reaction is often used for the selective chromatographic/spectrofluorimetric determination of selenium in water [42-44].

The work presented here is a preliminary, though fundamental, step to reach the ultimate goal of the designing of a new tool for onsite spectrophotometric determination of selenite ( $\text{SeO}_3^{2-}$ ). To achieve this goal, this paper will firstly be interested in optimization of the operating conditions to obtain a dedicated sorbent for selenite species (grafting of DAN onto Amberlite<sup>®</sup> XAD-4 resin beads via a diazo bridge) and will focus on the physical characterization of the support thus obtained (by TGA, Py-GC/MS and FTIR). The efficiency of the modified support has then tested by flow-through experiments in order to establish its chemical properties (selectivity, breakthrough volume and optimization of Se(IV) recovery procedure).

## **2. Experimental**

### **2.1. Materials**

Amberlite<sup>®</sup> XAD-4 resin was obtained from Acros Organics (Geel, Belgium). It was washed in methanol (24 h), 10% HCl aqueous solution (4 h), NaOH at pH 9 (4 h) and rinsed in methanol before drying at ambient temperature under reduced pressure. 2,3-diaminonaphtalene (DAN) was purchased from Acros Organics as well as all other chemical reagents.

### **2.2. Instrumentation**

Infrared spectra were taken using a Nicolet spectrometer (Thermo Scientific, Courtaboeuf, France). Resin samples were crushed before being pressed into KBr pellets. <sup>1</sup>H and <sup>13</sup>C NMR measurements were obtained on a Bruker 400MHz Ultrashield spectrometer. pH measurements of metallic solutions were performed with a digital pH meter (Metrohm 702).

Thermal analysis (DSC and TG) was carried out using a SDT Q600, NO32 device (TA Instruments, USA), using the following conditions: linear heating rate 10 °C/min from 30 to

800 °C, dynamic reconstituted air atmosphere, and sample weight approximately 7 mg. Py-GC/MS analysis (HP6890 (CPV) /HP5972A (SM), CP-SIL 8CB 30 m x 0,25 m x 0,25 µm CDS Analytical inc. column) were performed. Fractions of products (about 0.5 mg) were introduced into quartz tubes to be pyrolysed at 1000 °C for 15 s. The furnace settings for chromatography were: hold for 2 min at 50 °C and a ramp to 300 °C at a rate of 4°C/min.

An Inductively Coupled Plasma –Atomic Emission Spectrometry (ICP-AES) Jobin YVON JY2000 Ultratrace spectrometer (Les Ulis, France), equipped with a CMA spray chamber and a Meinhard TR50-C1 glass nebulizer (Courtaboeuf, France) was used to determine selenium amount. Determinations were performed according to the following operating parameters : power 1000W, pump speed 20 mL/min, plasma flow rate 12 L/min, coating gas flow rate 0.2 L/min, nebulizer flow rate 0.83 L/min, NaBH<sub>4</sub> 0.5% (m/v), NaBH<sub>4</sub> flow rate 0.8 mL/min and wavelength 196.03 nm. Sample solution and NaBH<sub>4</sub> solution were pumped to the nebulizer via Tygon tubing using a Minipuls™ 2 peristaltic pump (Gilson, Villiers-le-Bel, France).

### 2.3. Synthesis of EA-N<sub>2</sub>-DAN

414 mg (6 mmol) of sodium nitrite in 8 mL of deionised water were added drop-wise to a solution of 748 µL of 4-ethylaniline (6 mmol), 4 mL of deionised water and 1.86 mL of concentrated HCl (22.2 mmol) cooled by an NaCl-ice-water bath. The temperature was maintained at 0-5 °C during the addition. The disappearance of sodium nitrite was checked by potassium iodine starch paper then a cold solution of 2,3-diaminonaphtalene (950 mg) in CH<sub>3</sub>CN (108 mL) was added to the diazonium salt. The reaction mixture was stirred below 5 °C for 20 h. 1.37 mL of concentrated HCl was added to reaction mixture and EA-N<sub>2</sub>-DAN was filtered off and washed using 120 mL of cold CH<sub>3</sub>CN. EA-N<sub>2</sub>-DAN was stirred for 30 min in AcOEt (200 mL)/H<sub>2</sub>O (200 mL)/NaHCO<sub>3</sub> (1.5 g). After decantation, the organic layer was washed twice with 100 mL of 1.5% NaHCO<sub>3</sub> and twice by 100 mL of deionized water.

The organic layer was dried under  $\text{MgSO}_4$  and ethyl acetate was removed under vacuum. 1.33 g (yield 77.6%) of EA- $\text{N}_2$ -DAN was obtained as an orange powder.

$^1\text{H}$  NMR (DMSO  $d_6$ ,  $\delta$ , ppm) : 8.67 (l, 2H,  $\text{NH}_2$  ortho to  $\text{N}=\text{N}$ ); 8.57 (d, 1H, position 8 on naphthalene); 7.84 (d, 2H, meta to ethyl,  $J=8.27\text{Hz}$ ); 7.46 (dd, 1H, position 5 on naphthalene); 7.38 (d, 2H, ortho to ethyl,  $J=8.27\text{Hz}$ ); 7.24 (ddd, 1H, position 7 on naphthalene); 7.18 (ddd, 1H, position on 6 naphthalene); 6.98 (s, 1H, position 4 on naphthalene); 5.38 (s, 2H,  $\text{NH}_2$  meta to  $\text{N}=\text{N}$ ); 2.69 (q, 2H,  $\text{CH}_2$ ,  $J=7.6\text{Hz}$ ); 1.24 (t, 3H,  $\text{CH}_3$ ,  $J=7.6\text{Hz}$ ).  $^{13}\text{C}$  NMR (DMSO  $d_6$ ,  $\delta$ , ppm) (Scheme 1) : 151.4 ( $\text{C}_{11}$ ), 144.7 ( $\text{C}_{14}$ ), 136.8 ( $\text{C}_1$ ), 132.3 ( $\text{C}_2$ ), 128.7 ( $\text{C}_{13}$ ), 128.4 ( $\text{C}_4$ ), 127.5 ( $\text{C}_9$ ), 125.2 ( $\text{C}_3$ ), 125.1 ( $\text{C}_8$ ), 123.1 ( $\text{C}_6$ ), 122.9 ( $\text{C}_7$ ), 121.4 ( $\text{C}_{12}$ ), 120.7 ( $\text{C}_5$ ), 110.1 ( $\text{C}_{10}$ ), 28.0 ( $\text{C}_{15}$ ), 15.6 ( $\text{C}_{16}$ ). Elemental analysis: Calculated for  $\text{C}_{18}\text{H}_{18}\text{N}_4$  : C, 74.46%; H, 6.25% ; N, 19.29%. Found : C, 73.85%; H, 6.23% ; N, 19.25%. mp = 136 °C.

## 2.4. Synthesis and characterization of XAD4- $\text{N}_2$ -DAN

### 2.4.1. Amination of Amberlite® XAD-4

25 mL of sulfuric acid were slowly poured into 10 mL of nitric acid. 5.00 g of resin were slowly added in order to keep the temperature below 55 °C. The mixture was heated at 60 °C for 30 min. The solution was poured into 600 mL of iced water. 6.7 g of XAD4- $\text{NO}_2$  resin were filtered and washed with deionised water.

Resin XAD4- $\text{NO}_2$  (5.15 g, 28.7 mmol),  $\text{SnCl}_2$  (40 g, 21.1 mmol), concentrated hydrochloric acid (45 mL, 538 mmol) and ethyl alcohol (50 mL) were slowly stirred at 90 °C for 9 hours. After cooling, the resin was filtered. The resin was successively stirred with 250 mL of deionised water, 40 mL of  $\text{NaHCO}_3$ , 40 mL of 0.5 M NaOH and 50 mL of 2 M NaOH. It was then washed with deionised water (until pH of filtrate was neutral) and methyl alcohol. The brown resin XAD4- $\text{NH}_2$  (4.3 g) was dried under vacuum at room temperature.

### 2.4.2. Grafting of DAN

6.9 g (0.1 mol) of sodium nitrite in 40 mL of deionised water were added drop-wise to a solution of 1.03 g of resin XAD4-NH<sub>2</sub> in 100 mL 1.5 M HCl cooled at 0-5 °C. The temperature was maintained at 0-5 °C during the addition. The resin was held at 0-5 °C for 2 more hours while being stirred. It was then filtered, washed with cold water and maintained below 5 °C. A cold solution of 2,3-diaminonaphthalene (1.0 g) in CH<sub>3</sub>CN (117 mL), deionised water (13 mL) was added to the resin. The reaction mixture was stirred below 5 °C for 48 h. The resin XAD4-N<sub>2</sub>-DAN was filtered off and washed by CH<sub>3</sub>CN, NaHCO<sub>3</sub> 5%, deionised water and methyl alcohol. The dark red resin XAD4-N<sub>2</sub>-DAN was dried under vacuum at room temperature.

#### **2.4.3. Grafting rate**

The grafted sorbents (approximately 50 mg) were put in 50 mL of 5.10<sup>-3</sup> M HClO<sub>4</sub> aqueous solution for 72 h. After filtration, 5 mL of the filtrate were diluted with 35 mL of deionised water and titrated by a 5.10<sup>-3</sup> M NaOH solution. The original acidic solution was also titrated by the 5.10<sup>-3</sup> M NaOH solution. The sorbents were regenerated with a 5% NaHCO<sub>3</sub> solution.

#### **2.4.4. Water uptake**

The resins were put in deionised water at room temperature for 4 h with orbital agitation. They were quickly filtered and dried under ambient temperature and atmospheric pressure for 24 h. TG analysis was performed to determine the water uptake capacity: isotherm at 110 °C for 60 min (stabilisation of weight loss).

### **2.5. Sorption and recovery of Se(IV)**

Solid Phase Extraction of Se(IV) was studied in flow experiments according to the conditions presented below.

#### **2.5.1. Column preparation**

50 mg of synthesized resin were weighed and packed between 2 frits into a Methyl Polymetacrylate micro-column of 6 mm inner diameter and 10 mm length (Supelco), affording thus flow-through percolation of samples. The resin was cleaned into the column by passing 50 mL of 1 M sodium hydroxide, 50 mL of MilliQ water and 50 mL of 1 M hydrochloric acid (Plasma pure grade, SPS Science). Finally, 50 mL of MilliQ water was passed through the column to elute out excess acid.

### **2.5.2. Testing solutions**

Testing solutions of varying concentrations of selenium(IV) were prepared by diluting the stock solution (1 g/L) in Milli-Q water. The pH of these testing solutions was adjusted by adding hydrochloric acid or NaOH solutions.

### **2.5.3. Procedure**

The columns were placed in a micro-column oven in order to control the temperature during SPE experiments. 25 mL of testing solutions described above were passed through the columns at varying flow rates controlled by a peristaltic pump (IPC8, Ismatec, Glattbrugg, Switzerland). Consequently, a 25 mL aliquot of eluent was used to elute the columns at varying flow rates. All solutions were analysed by ICP-AES.

## **3. Results and discussion**

### **3.1. Synthesis of EA-N<sub>2</sub>-DAN**

Grafting a ligand on a reticulated polymer implies that the reactions occur in a heterogeneous phase which makes it difficult to characterise the grafted polymers: those materials are insoluble in all organic solvents. For this reason, we decided to first achieve the grafting on a molecule in order to be able to use classical techniques of characterisation in organic chemistry (such as NMR). The aim is first to prove that the chosen synthetic scheme is achievable, then to optimise the experimental conditions on a molecular scale and finally to

use characterisation (for example by FTIR) of the molecular product to help characterisation of the modified sorbent.

In this paper, we propose the grafting of DAN on Amberlite® XAD-4 resin via a diazo bridge. This sorbent is mainly composed of poly(ethylvinylbenzene-*co*-divinylbenzene). To represent this copolymer, a benzene entity was chosen, bearing an amine function for the formation of diazo link. 4-ethylaniline was selected since the ethyl group makes integration of  $^1\text{H}$  NMR signal easier.

The synthetic route with formation of a diazonium salt is proposed in scheme 2. Several experimental conditions were tried (Table 1) to study the influence of the quantity of hydrochloric acid, the mixing diazonium salt with DAN and the medium for introducing DAN. The reaction of diazoic coupling with DAN does not occur if DAN is introduced in aqueous or hydroalcoholic phase: DAN is only soluble in presence of excess hydrochloric acid which deactivates the naphthalene group by protonation of amine function and prevents coupling reaction. A new way for introducing the aromatic compound has been perfected by using acetonitrile as dissolving agent. Best yields are obtained when DAN solution is added on diazonium salt : attempt 3 compared to 4. Finally, modifying aqueous media/acetonitrile rate does not significantly affect reaction yield but excess of acetonitrile is favourable for grafting on polymer sorbents which are intrinsically hydrophobic.

The formation of diazonium link was possible on position 1, 5 or 6 of the naphthalene group :  $^1\text{H}$  NMR analysis proved that it occurred on position 1 by the presence of a singlet peak at 6.98 ppm. Final attribution of  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra was achieved through COSY, NOESY, HMBC, HMQC experiments. FTIR analysis of EA-N<sub>2</sub>-DAN evidenced N=N stretching vibration at 1604  $\text{cm}^{-1}$ , C-N stretching vibration at 1277  $\text{cm}^{-1}$ , C-H deformation of a 1:4 disubstituted aromatic group (bearing ethyl function) at 744  $\text{cm}^{-1}$  and replacement of 870

$\text{cm}^{-1}$  intense peak (1:2:4:5 tetrasubstitution on an aromatic ring) of DAN by a weak peak at  $879 \text{ cm}^{-1}$  corresponding to 1:2:3:4:5 pentasubstitution on an aromatic ring.

The presence of two amine functions and a diazo bridge in EA-N<sub>2</sub>-DAN might give rise to three basic sites for this molecule. However, considering the two pK<sub>A</sub> values of DAN : 0.50 and 2.11 [45], it seems reasonable to forecast only two basic functions for EA-N<sub>2</sub>-DAN. This was confirmed by <sup>1</sup>H NMR of EA-N<sub>2</sub>-DAN put in contact with an excess of hydrochloric acid. The spectrum showed the presence of only two more protons on the molecule.

### 3.2. *Synthesis and characterization of XAD4-N<sub>2</sub>-DAN*

Grafting of DAN on Amberlite<sup>®</sup> XAD-4 was achieved in three steps according to scheme 3. The quantity of sodium nitrite introduced for the formation of the diazonium salt (XAD4-N<sub>2</sub><sup>+</sup>) was first followed by use of potassium iodine starch paper. This method appeared to be limited by the slow kinetics of the reaction. Introducing nitrite sodium in excess proved to be more efficient. Anyway, it was important for grafting of DAN to avoid excess of nitrite since DAN can easily form a naphthotriazole by reaction with nitrites in acidic medium [39, 40]. For this reason, after diazonium formation and before coupling with DAN, sorbents were extracted from reaction mixture and rinsed with cold water.

Thermogravimetric analyses were performed on XAD4-NH<sub>2</sub>, XAD4-N<sub>2</sub>-DAN, DAN and mixture of XAD4-NH<sub>2</sub> with DAN ( Fig. 1) under air atmosphere. DAN thermogram presented an important weight loss at 195 °C. For XAD4-NH<sub>2</sub>, degradation began at 350 °C by depolymerisation and simultaneous oxidation of the resin [46] and was followed at 485 °C by degradation of aromatic rings. Mixture of XAD4-NH<sub>2</sub> and DAN was characterised, as expected, by the three previous phenomena : degradation of DAN (195 °C), depolymerisation (350 °C) and degradation of aromatic rings (485 °C). In the case of XAD4-N<sub>2</sub>-DAN, no weight loss was observed before depolymerisation at 350 °C proving that if DAN is present

on this resin it is not impregnated. Moreover, degradation of aromatic rings occurs on a wider range of temperature (from 485 to 610 °C).

Py-GC/MS analysis on XAD4-N<sub>2</sub>-DAN confirmed the presence of DAN as a degradation product ( $t_R = 35.15$  min) and of azaphenanthrene as a rearrangement product issued from diazoic compound ( $t_R = 34.5$  min).

FTIR analysis was used to evidence chemical modifications of sorbents. Characterisation of XAD4-NO<sub>2</sub> and XAD4-NH<sub>2</sub> resins by FTIR was previously achieved [22]. Fig. 2 presents FTIR spectra of DAN, XAD4-NH<sub>2</sub> and XAD4-N<sub>2</sub>-DAN. The grafting of DAN enhanced the C-N stretching band at 1277 cm<sup>-1</sup>. As for EA-N<sub>2</sub>-DAN, the peak at 870 cm<sup>-1</sup> for DAN was shifted at higher wavelengths: 883 cm<sup>-1</sup> (pentasubstitution of an aromatic ring). The band at 949 cm<sup>-1</sup> (aromatic ring) present on the DAN spectrum was no longer observable on XAD4-N<sub>2</sub>-DAN spectrum. The disappearance of bands at 710 and 798 cm<sup>-1</sup> of XAD4-NH<sub>2</sub> was also observed with appearance of a band at 756 cm<sup>-1</sup>. Even though it was not possible to observe the N=N stretching vibration because of an intense peak at 1620 cm<sup>-1</sup> (C=C aromatic), previous observations confirmed that DAN was grafted on XAD4-NH<sub>2</sub>.

Acido-basic back titration of XAD4-N<sub>2</sub>-DAN was used to estimate the quantity of grafted DAN since direct titration was impossible because of too long equilibration periods. The study of EA-N<sub>2</sub>-DAN molecule proved that it presented two basic functions (diazo link and one amine group). This information was used to calculate the amount of DAN per gram of resin : this was found to be 0.48 mmol/g.

Finally, the water uptake was measured from thermogravimetric analysis of humidified resins at 110 °C [47]. As expected Amberlite® XAD-4 proved to be hydrophobic, retaining less than 1% of water. The increase of the weight loss with functionalization was in agreement with an increase of the hydrophilicity of the sorbents by introduction of hydrophilic functions : first, one amino group for XAD4-NH<sub>2</sub> (WR = 8%) and two for XAD4-

N<sub>2</sub>-DAN (WR = 14%). This improvement of hydrophilicity will be favorable to the interaction of modified sorbents with an aqueous phase.

### 3.3. Retention properties

#### 3.3.1. Sorption of Se(IV)

2,3 diaminonaphthalene is a well known ligand for the complexation of Se(IV) in organic solvent at pH 2. In aqueous medium, Se(IV) slowly reacts with DAN at room temperature and a heating stage is usually required to complete the reaction within some minutes [48]. We studied these two parameters (pH and temperature) in order to check if the behaviour was the same on solid phase. 25mL of 100 µg/L Se(IV) were percolated through modified resin column at varying flow rates, pH and temperature values in order to test the sorption of selenium.

Our results show that Se(IV) can be removed from the samples if the pH value is fixed between 1.5 and 2 and sample heated to 80 °C. These results are consistent to the pK<sub>A</sub> values of selenious acid and DAN. The pK<sub>A1</sub> and pK<sub>A2</sub> of selenious acid are 2.46 and 7.31, respectively and those of DAN are 0.5 and 2.11 [45]. The piazselenol (naphto-2-selena-1,3-diazole) is formed in a reaction between undissociated selenious acid and single-protonated DAN (Scheme 4). The theoretical optimal range of pH values for the formation of piazselenol is thus between 1.5 and 2. For a temperature of 80 °C, retention rates of selenium were 88 and 82% for pH values fixed to 2 and 1.5 respectively. Higher and lower pH values decrease retention rates. Temperature also directly influences retention rate of Se(IV). A low temperature involves a slow reaction time and the Se–DAN complex decomposes at high temperatures.

For optimal conditions (pH 2; temperature fixed to 80 °C), Fig. 3 shows that the influence of flow rate on the sorption of Se was significant. The preliminary tests showed that only 40%

of Se(IV) was removed from the testing solution at a flow rate of 1.5 mL/min. The retention rate was improved to about 88%, when the flow rate was reduced to 0.6 mL/min. The flow rate of 0.6 mL/min was thus used for the following tests.

### 3.3.2. Recovery and capacity tests

Experiments using 25mL of 100 µg/L Se(IV) standard solution were conducted in triplicate to examine the recoveries of Se(IV) from modified resin by various eluent solutions. The results show that Se(IV) was not effectively recovered by a 0.1 M HCl solution ( Fig. 4). Thiol compounds are known to react with Se(IV) to form selenotrisulfides and induce a competitive reaction with DAN. Cysteine (0.1 M; pH 7) and bismuthiol II (0.1 M; pH 2) were thus tested as eluent solutions to remove Se(IV) from the synthesized XAD4-N<sub>2</sub>-DAN resin. The recovery of Se(IV) was compared to that obtained with sodium borohydride (0.5% in 0.5M NaOH). Results show that cysteine allowed complete elution (96%) of Se(IV) while bismuthiol II and sodium borohydride led to the recovery of 85% and 45% of Se(IV) respectively.

The capacity of the resin was determined in flux experiment by passing one litre of a Se(IV) solution (600 µg/L) through the column by fractions of 50 mL. Each fraction was analysed to determine Se(IV) retained onto the synthesised resin. Capacity of the XAD4-N<sub>2</sub>-DAN resin column was determined to be 3.4 mg/g for Se(IV) under the study conditions (pH 2; 80 °C; flow rate=0.6 mL/min).

### 3.3.3. Interferences

Interference experiments of other metals and anions were conducted in triplicate in this study. Interference regarding major anions (F<sup>-</sup>, Cl<sup>-</sup>, PO<sub>4</sub><sup>3-</sup>, SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>) is negligible (< 5%) for concentrations up to 250 mg/L. Nitrite anion reacts with DAN but interfere in Se(IV) quantification (>7%) for concentrations above 2.5 mg/L. Concerning metals, experiments were carried out using a multi-element solution (200 µg/L for each metal). Fig. 5 presents the

retention profile of each studied interfering metal on the modified resin according to pH values. The results show the selectivity of XAD-N<sub>2</sub>-DAN modified resin for the extraction of Se(IV) at low pH. For a pH value equals to 2, only 30% of copper are retained. This interference can be limited by adding 0.01 M EDTA to the sample before percolation of the sample through the column.

### **3.4. Application**

The performance of the proposed grafted resin and the proposed extraction/elution optimized procedure (Scheme 5) was examined by determination of total selenium in certified reference wastewater materials (BCR-715). The results are given in Table 2. 32 µg/L has been determined by taking into account the 88% sorption rate of Se(IV) onto the modified resin and the 96% recovery rate of Se(IV) during the elution step with 0.1 M cysteine. The results show that this system provided analytical data within the ranges of the certified values.

## **4. Conclusion**

A new chelating resin bearing 2,3-diaminonaphthalene (DAN) has been synthesized by grafting DAN on Amberlite® XAD-4. First, DAN was grafted via a diazo bridge at a molecular level on 4-ethylaniline (EA-N<sub>2</sub>-DAN) for optimization purposes. <sup>1</sup>H NMR of EA-N<sub>2</sub>-DAN evidenced that the coupling occurs on first position of DAN. The synthesis and characterization of this model compound facilitated FTIR spectra analysis for XAD4-N<sub>2</sub>-DAN by emphasizing characteristics bands. The efficiency of the grafting has been assessed by TGA, Py-GC/MS and FTIR: the use of these three methods proved that DAN was not only impregnated but covalently linked to the resin. The amount of grafted DAN has been quantified by back titration and was found to be 0.48 mmol/g. This amount may be compared to the resin capacity determined at 3.4 mg/g of Se(IV), i.e. 0.043 mmol/g of Se(IV). The reaction between DAN and Se(IV) is known to be stoichiometric in liquid medium. In our

case, during a solid-liquid reaction between DAN and Se(IV), the stoichiometric ratio seems to be 10:1 (DAN:Se) but, at this stage of research, the only conclusion is that less than 10% of the complexing sites are accessible to metalloid ions.

The complexation capacity of the grafted sorbent has been evaluated through flow-experiments with standard solution of  $\text{SeO}_3^{2-}$ . At a flow rate of 0.6 mL/min, a 88% retention rate of selenium has been observed at pH 2.0 and 80 °C. This retention rate has proven to be reproducible (when amount of Se(IV) is between 5 and 100  $\mu\text{g/L}$ ).

The resin XAD-4 thus modified with DAN has proven to be selective towards Se(IV). The adjustment of this modified sorbent, packaged in a micro-column, for a direct fluorimetric selenium determination is currently being investigated.

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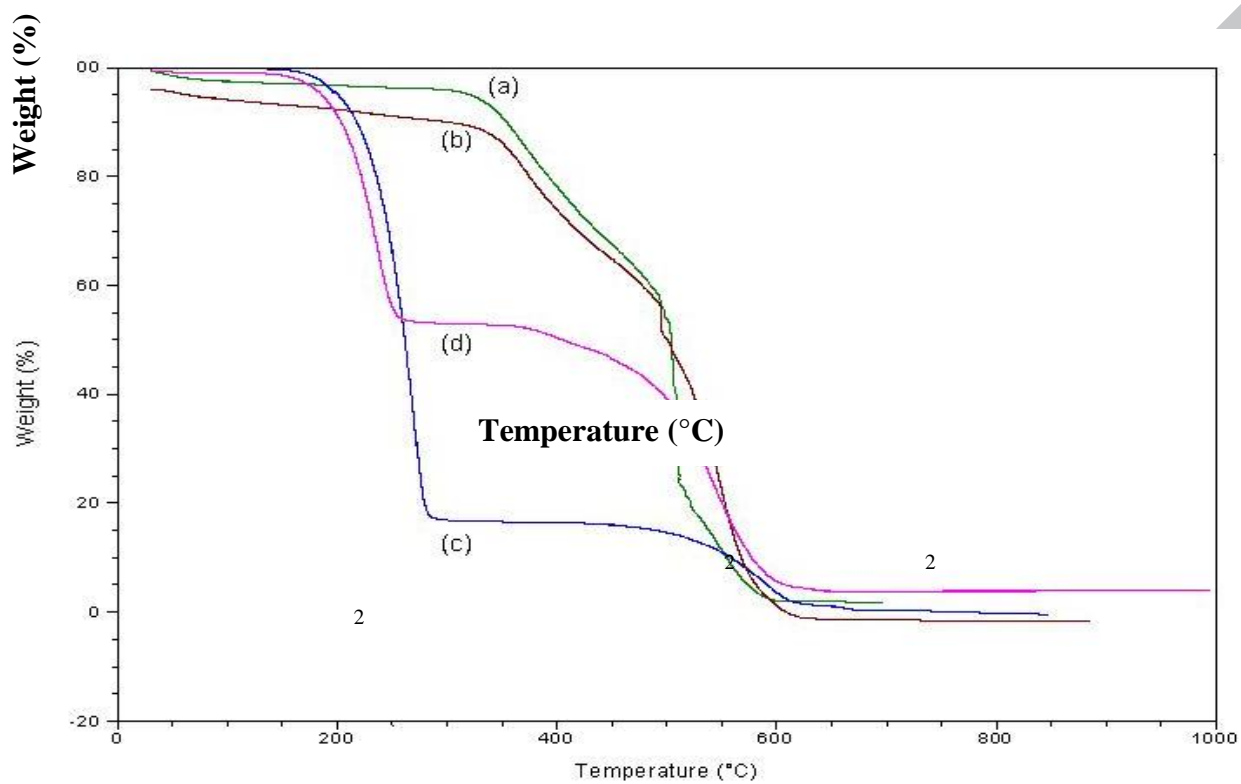
Experiment number	HCl quantity	Solvent for DAN	Addition order	V <sub>H2O</sub> /V <sub>CH3CN</sub>	Yield
1	>25 eq	Aqueous HCl	Diazonium on DAN	1/0	/
2	>25 eq	EtOH/Aqueous HCl	Diazonium on DAN	1/0	/
3	2.7 eq	CH <sub>3</sub> CN	Diazonium on DAN	6,5/10	57%
4	2.7 eq	CH <sub>3</sub> CN	DAN on Diazonium	7,5/11	85%
5	3.7 eq	CH <sub>3</sub> CN	DAN on Diazonium	12/108	78%

Table 1 : Experimental conditions for preparation of EA-N<sub>2</sub>-DAN

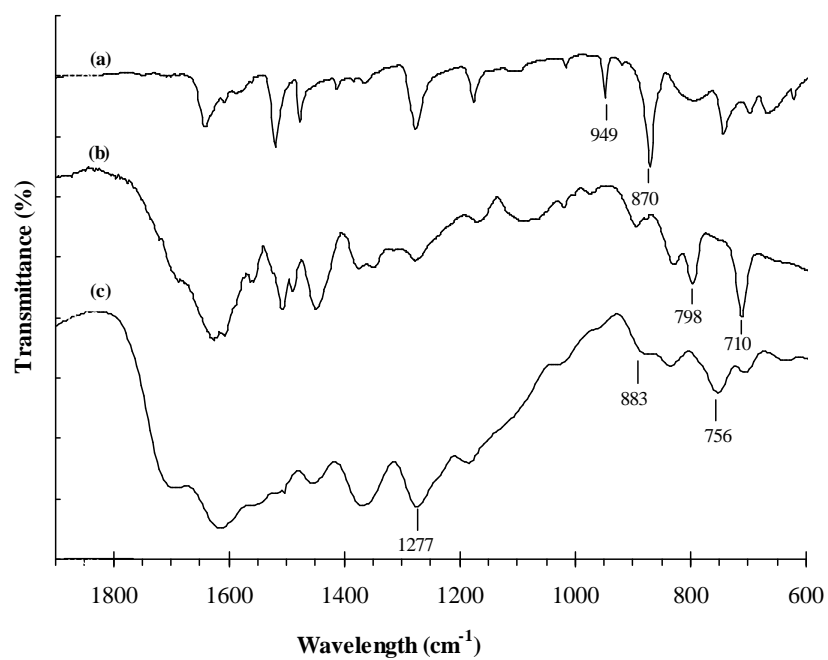
Sample	BCR-715 (Wastewater - Industrial effluent)
Certified ( $\mu\text{g/L}$ )	$29 \pm 4$
Found ( $\mu\text{g/L}$ )	$31 \pm 2$
Recovery (%)	107

**Table 2.**

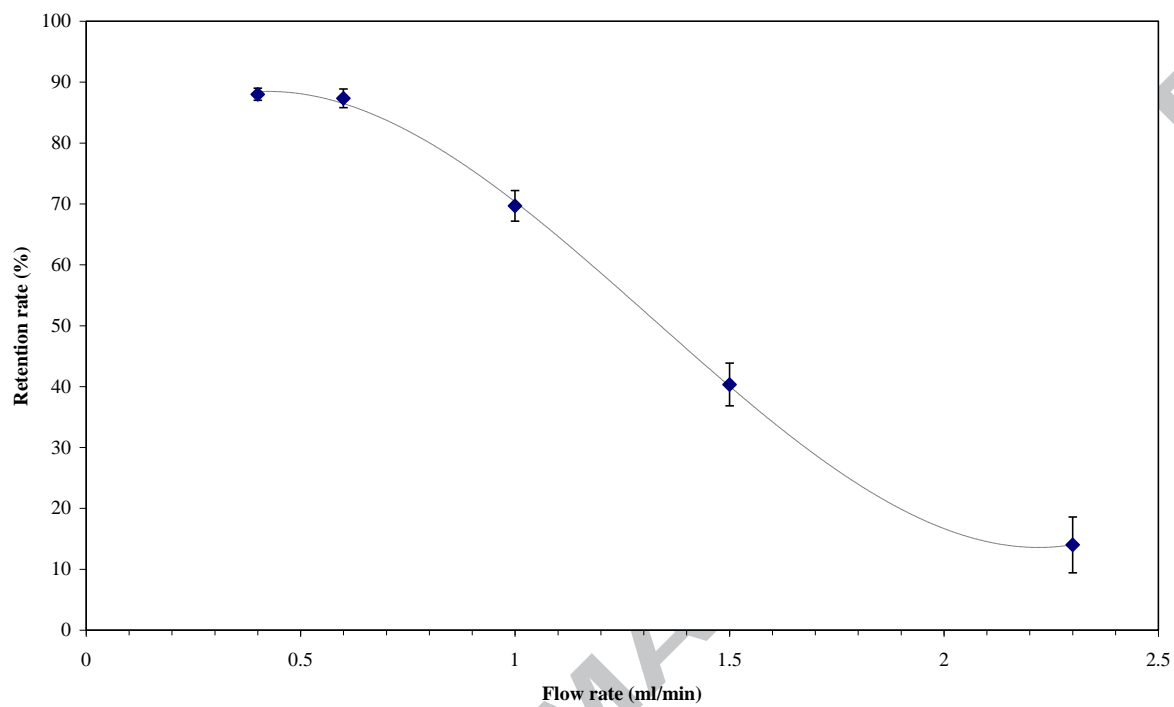
The level of total selenium in the standard reference material after application of the presented procedure



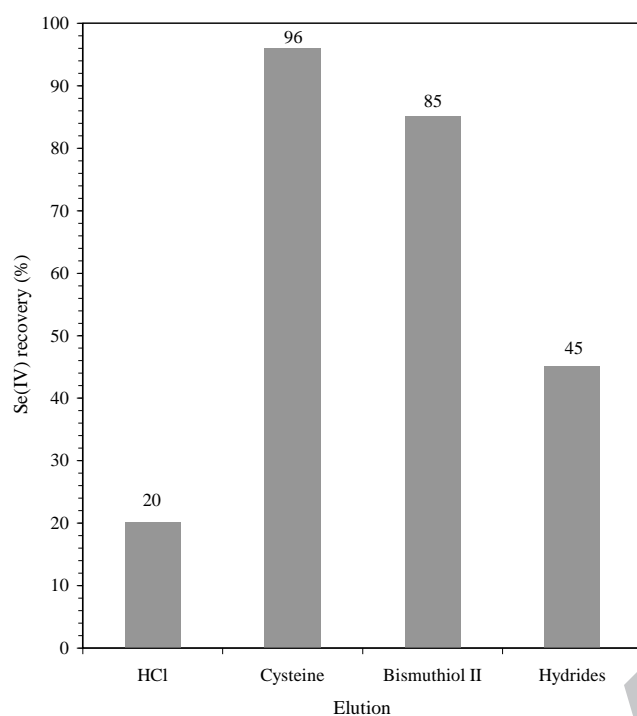
**Fig. 1.** Thermogravimetric analysis of XAD4-NH (a), XAD4-N -DAN (b), DAN (c) and mixture of XAD4-NH with DAN (d) performed under air atmosphere (heating rate = 10 °C/min)



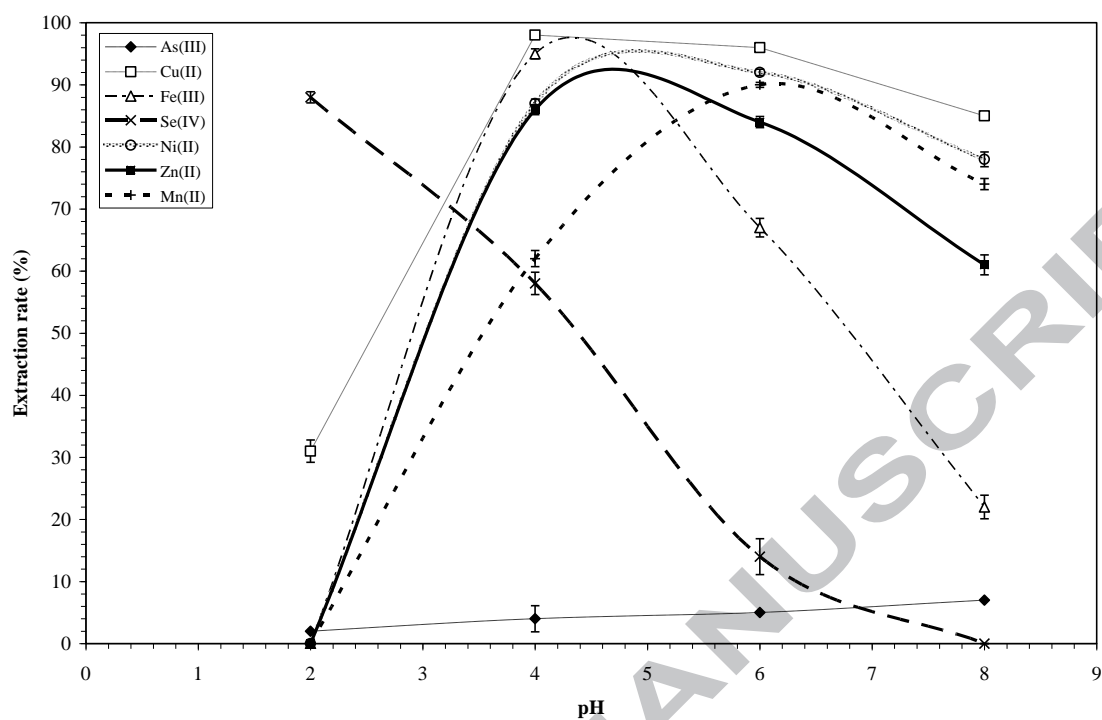
**Fig. 2.** FTIR spectra of DAN (a), XAD4-NH<sub>2</sub> (b) and XAD4-N<sub>2</sub>-DAN (c) (KBr pellets)



**Fig. 3.** Retention rate of Se(IV) versus percolation flow rate (Se(IV) = 100  $\mu\text{g/L}$  at pH 2.0; Temperature fixed at 80  $^{\circ}\text{C}$ )

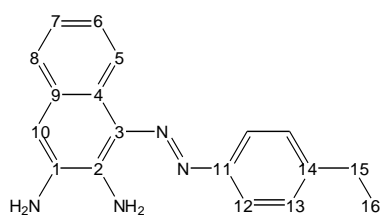


**Fig. 4.** Recovery rate of Se(IV) previously retained onto modified resin with different eluents (all eluents are at a  $0.1 \text{ mol.L}^{-1}$  concentration, except sodium borohydride : 0.5% in NaOH 0.5 M)

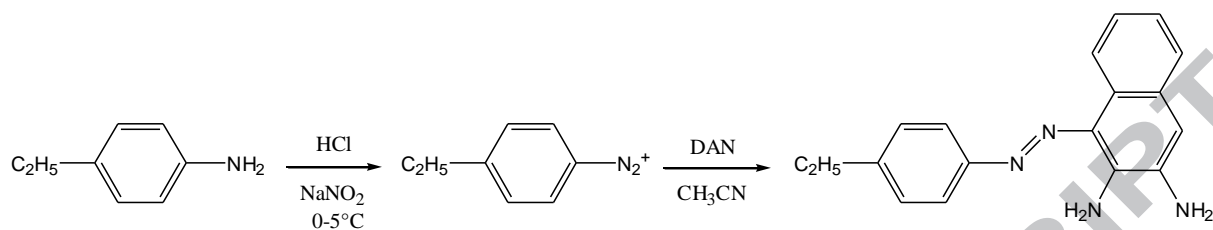


**Fig.5.** Study of potential interferences on Se(IV) sorption onto modified resin

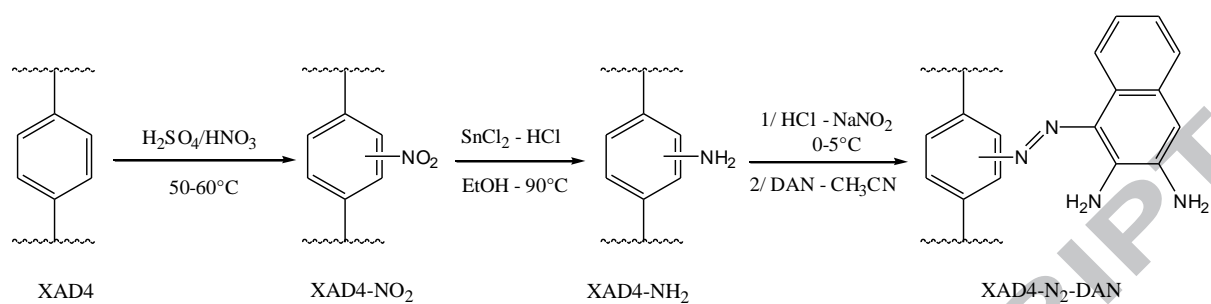
(All metals tested are at a 200  $\mu\text{g/L}$  concentration. Elution experiments were conducted at 80  $^{\circ}\text{C}$  and at a constant flow rate of 0.6 mL/min)



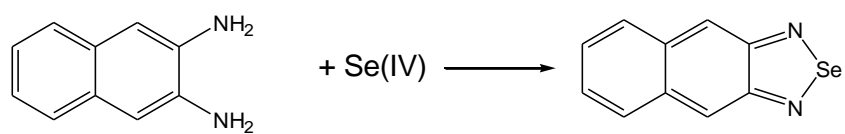
**Scheme 1** : Indexation of the different carbons of EA-N<sub>2</sub>-DAN for <sup>13</sup>C NMR



Scheme 2 : Synthesis of EA-N<sub>2</sub>-DAN

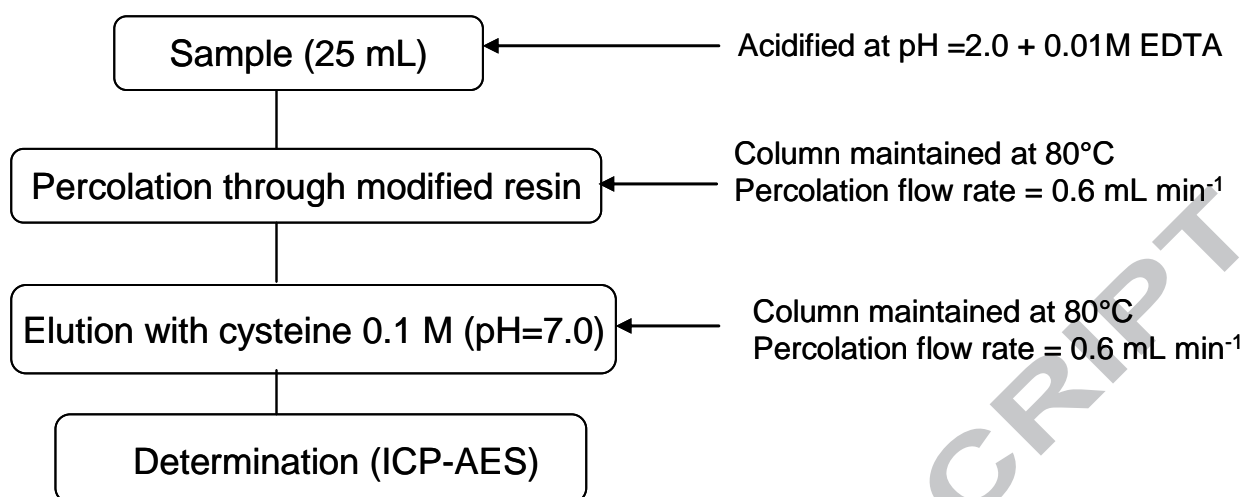


**Scheme 3 :** Synthesis of XAD4-N<sub>2</sub>-DAN



**Scheme 4.** Formation of piazselenol (naphtho-2-selena-1,3-diazole)

ACCEPTED MANUSCRIPT



Scheme 5 : Optimized procedure for the determination of Se(IV)