Journal Academica Vol. 2(3), pp. 170-184, December 31 2012 - Environmental Science - ISSN 2161-3338
online edition www.journalacademica.org © 2012 Journal Academica Foundation

Full Length Research Paper

Elaboration of Surface Plasmon Resonance Sensor Based on Calix[4]Arene Self-Autoassembeld Monolayer of Cysteamine for Heavy Metals Detection in Water

Messaoud Benounis *
Laboratory of Sensors, Instrumentation and Process (LCIP), Institute of Science and Technology, University of Khenchela, Khenchela, (Algeria)

Accepted December 30 2012

ABSTRACT

In this work, a new chromogenic calix[4]arene was functionalized onto self-autoassembled monolayer of cysteamine for heavy metals detection and tested by using SPR measurement. To functionalize SPR sensor, two procedures were proposed. The first is based on the oxidation of calixarene-SAM alcohol group to quinone. In the second procedure, pyridine was made to protect oxygen donor group and catalyse the reaction between SAM and calixarene alcohol group. Heavy metals were used Cu^{+2}, Co^{+2}, Cd^{+2}, Mg^{+2}. Detection limit reached are lower than 10^{-5}µM for the most heavy metals. PH of detection was optimised for each ion and detection was made in basic solution. Several detection zones were observed and linear sensitivities were showed for different heavy metals detection at different zones. The sensitivities obtained are 151.46, 210, 103.99 and 43.75µM^{-1} for M, Co^{+2}, Cu^{+2} and Cd^{+2}, respectively.

Key words: calxarene, SAM, SPR, ions, heavy metals, sensor, sensitivity

1. INTRODUCTION

Calixarenes are currently the subjects of study as chemical sensors and selective receptors due to their important functionalisation and complexations possibilities. Among this sensors, different calixarene derivative may be found, thanks of their importance in the fields the medicine and the environment, in ions selective electrodes and in chromogenic sensors (David, 1989; Antesberger et al., 2005; McMahon et al., 2003; F.F. Nachtigall et al., 2002; Atwood et al., 2002; Thallapally et al., 2005; Purse et al., 2005; Kumar, et al., 2006).

Many work was carried out based on calixarene molecule using polymer support and different measurement techniques to detect traces of ions were reported (Jain et al., 2005; Lu et al., 2004; Duncan and Cockayne, 2001; Pérez-Jiménez et al.,1998; Chen et al., 2000; Bouazizi et al., 1996; Lu et al., 2002). A Poly(vinyl chloride) (PVC) based membrane calixarene was largely used to ions and heavy metals detection (Jain et al., 2005; Lu, et al., 2004; Duncan and Cockayne, 2001; Pérez-Jiménez et al., 1998; Chen et al., 2000). For example, it is used as CrO2-4 selective sensor (Jain et al., 2005), silver ion selective electrode (Duncan and Cockayne, 2001, Chen et al., 2000) and caesium-selective sensor (Pérez-Jiménez et al., 1998).

---

*Corresponding author: benounis@yahoo.fr

The use of polymer as support for calixarene, decrease the sensitivity of the sensor (Levit et al., 2002; Park et al., 1999). It is shown that surface adsorption and bulk adsorption of polymers affect the sensitivity and the response time of sensor and exhibiting low vapour permeability. Therefore, we are directed to another effective functionalization technique largely used for self-autoassembled monolyer (SAM). The advantages of SAMs include simplicity of preparation, versatility, stability, reproducibility and the possibility of introducing different chemical functionalities with high-level of order on a molecular dimension (Ulman, 1991; Gao and Siow, 1996; Aizenberg et al., 1998; Sat et al., 1996). One of the most widely used systems in the molecular self-assembled method is the chemisorption of sulfur derivatives (i.e. thiols, disul- fides) on gold surfaces (Steinberg and Rubinstein, 1992; Mandler and Turyan, 1996; Flink et al., 1998).

There are several reports on the use of SAMs to improve selectivity and/or sensitivity of gold electrodes in a broad range of electro-analysis. A feasible method of fabricating phthalocyanine sensors was developed by a covalent attachment of cobalt tetracarboxylic acidchloride phthalocyanine (CoTCACIPc) onto a preformed 2-mercaptoethanol (2-ME) self-assembled monolayer (SAM) modified gold electrode (designated as CoTCACIPc-2-ME-SAM) (Mashazi et al., 2007). Concentration range 0.28^{-20} µM with a detection limit of 5×10^{-7} M. Copper sensors based on SAM were developed (Freire and Kubota, 2004; Arrigan, Bihan, 1999). In reference (Freire and Kubota), a gold-electrode modified with a self-assembled monolayer (SAM) of 3-mercaptopropionic acid (MPA) was evaluated a highly sensitive voltammetric sensor for copper ions. The detection limit reached 1.8 10^{-14}M for copper. In (Arrigan and Bihan, 1999), reported a cysteine monolayer-coated gold-electrode and its Cu^{2+} complexation, which allowed a detection of Cu^{2+} down to 10^{-7}M. A selective molecular interaction at an interface formed by self-assembly of a macrocyclic synthetic host, calyx[4]resorcinarene with four thiol groups (R4SH) were investigated [Faull, Gupta, 2003]. They demonstrated that the noncovalent chemical selectivity of SAMs of hosts calyx[4]resorcinarene extends to isomers of several different guest molecules. A selective Quinone-functionalised calix[4]arenes having carboxylic acid groups or thiol groups were prepared (Parket al., 2001). The sensors exhibited a selective affinity towards specific hard-metal ions in aqueous media.

Surface-plasmon waves (SPWs) are extremely sensitive to small changes in the refractive index near the sensor surface and the changes in the refractive index are proportional to the sample mass, so the adsorption of molecules on the metal film or conformational change in the adsorbed molecules can be detected accurately (Boussaad et al., 2000; Zacher, Wischerhoff, 2002; Georgiadis et al., 2000; Sarkar, Somasundaran, 2003; Chah et al., 2002). In these works, a chromogenic calix[4]arene molecule was immobilized onto modified SAM gold surface of an SPR sensor chip for heavy metals detection. Two functionalized procedures were proposed. The first is based on the oxidation of calixarene-SAM alcohol group to quinone. In the second procedure, pyridine was made to protect the oxygen donor group and to catalyze the reaction between SAM and the calixarene alcohol group.

2. EXPERIMENTAL

2.1 SPR Material and Principle

Surface Plasmon Resonance Spectrometer BIO-SUPLAR 2 (Analytical μ-Systems, Germany) produced by Biacore company was used. It is based on the Kretschmann type prism and GaAs solid-state laser (λ= 670nm).

The SPR detection-principle is constituted by measurement of the intensity of the reflected light. At the SPR-angle, a sharp decrease or 'dip' of intensity is measured. The position of the SPR-angle depends on the refractive index in the substance with a low-refractive index close to the sensing surface. The refractive index near the sensor surface changes, because of ions binding to the surface. As a result, the SPR-angle will change according to the amount of bound ions.

During a binding analysis, SPR changes occur as a solution is passed over the surface of a sensor chip. To perform an analysis, one interactant is captured on a sensor surface. The sensor surface forms one wall of a flow cell. A sample containing the other interactant(s) is injected onto this surface in a precisely controlled flow. Fixed wavelength light in a fan-shaped form is directed at the sensor surface and molecular binding events are detected as changes in the particular angle where SPR creates extinction of light. This change is measured continuously to form a sensorgram (Fig. 1), which provides a complete record of the progress of association or dissociation of the interactants.

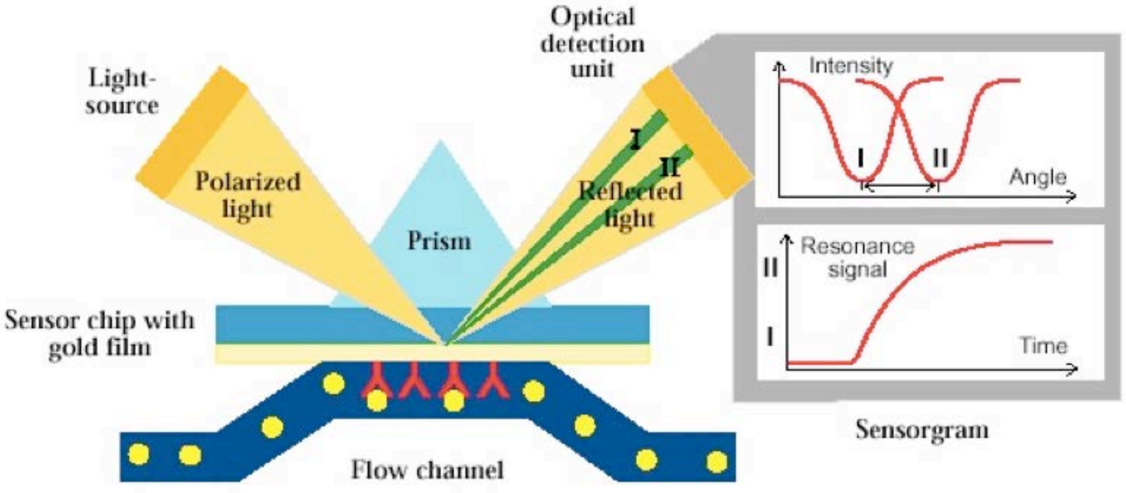


Figure 1 SPR sensing principle

2.2 Synthesis of the chromogenic amide derivative calix[4]arene

The synthesis of tetra-O-substituted calix[4]arene derivative was performed by the reaction sequence depicted in Figure 2. The treatment of p-tetrakis(phenylazo)calix[4]arene with tertiary acetamide (α-chloro-N,N-diethylacetamide) in the presence of CaH_2 as base gave p-tetrakisphenylazocalix[4]arene tetra-amide derivative in cone conformation (Halouani et al., 2002).

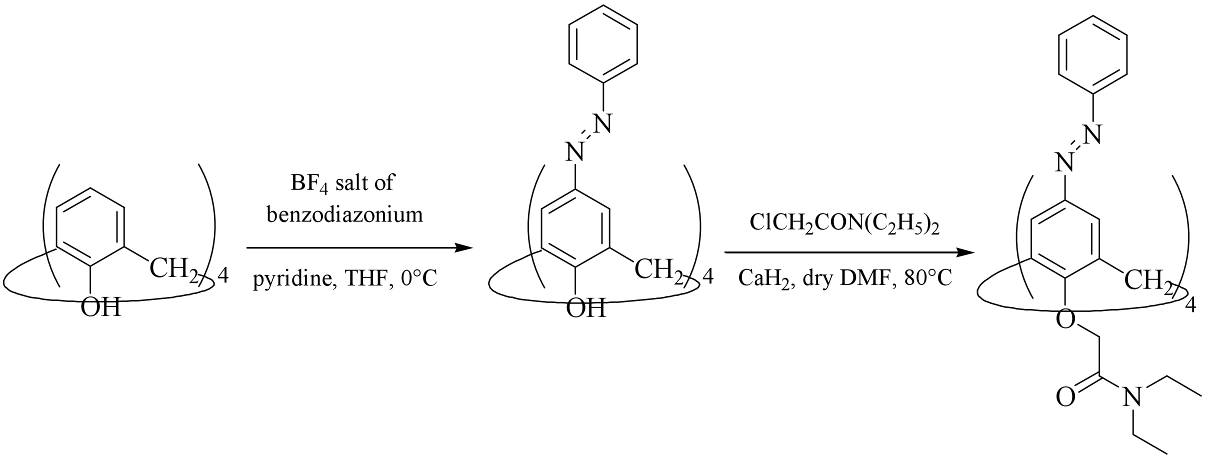


Figure 2 Reaction sequence for the synthesis of p-tetrakisphenylazocalix[4]arene tetra-amide derivative.

2.3 Reagents and samples preparation

Several samples necessary to elaborate the sensor were prepared. First, 10^{-2} M of cysteamine solution was prepared in which a sensor was immersed. Calix[4]arene solution was prepared by dissolved 5mg of calix[4]arene powder in 2ml of chloroform. Calix[4]arene was deposited on the sensor by dip-coating technique. This technique makes it possible to have homogeneous layers. PCC or pyridinium chlorochromate, known as *Corey's Reagent* (Corey and Suggs, 1975), was prepared. To 22ml of 6M HCl 12g of CrO3 were added. After ultrasonic mixing for 10min., 9,5g of pyridine were added to the homogeneous solution. Ultrasonic mixing over 5min. and cooling to 0 °C. A dilute sulfochromic oxidant solution and aqueous solutions containing 0µM to 1µM of the metal ions Cu^{+2}, Co^{+2}, Cd^{+2} and Mg^{+2} were prepared. Phosphate buffer solution PBS was prepared at pH = 8.

2.4 Immobilization of calix[4]arene on the Self-autoassembled monolyer of cysteamine onto gold surface

A principle scheme for the functionalization of calix[4]arene-SAM onto a gold surface for ions detection is presented in Fig. 3:

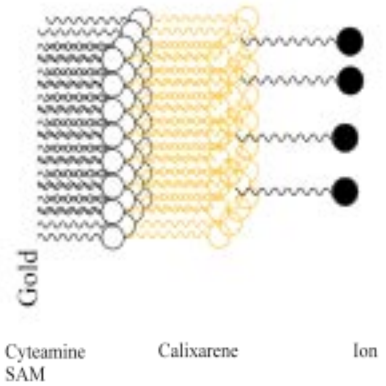


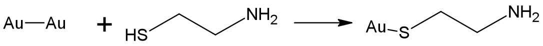
Figure 3 SAM-Calix[4]arene scheme for ion detection.

To functionalize a SPR the sensor, two procedures were proposed:

First procedure steps:

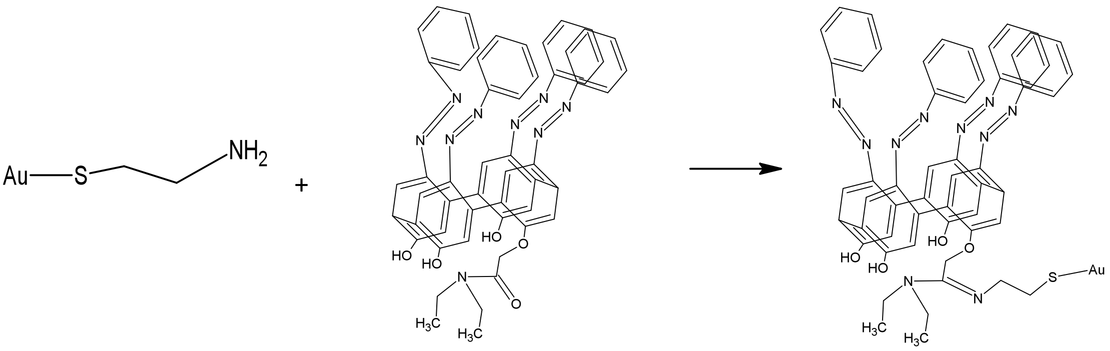
In the first procedure, five stages are necessary:

1. In SPR the adhesion between the gold layer and glass is only physical. Pirhana was not made to clean the gold surface. Accordingly, acetone and ethanol were used.
2. Grafting of SAM on the gold surface: The sensor is immersed in 15mM of cysteamine during two hours.

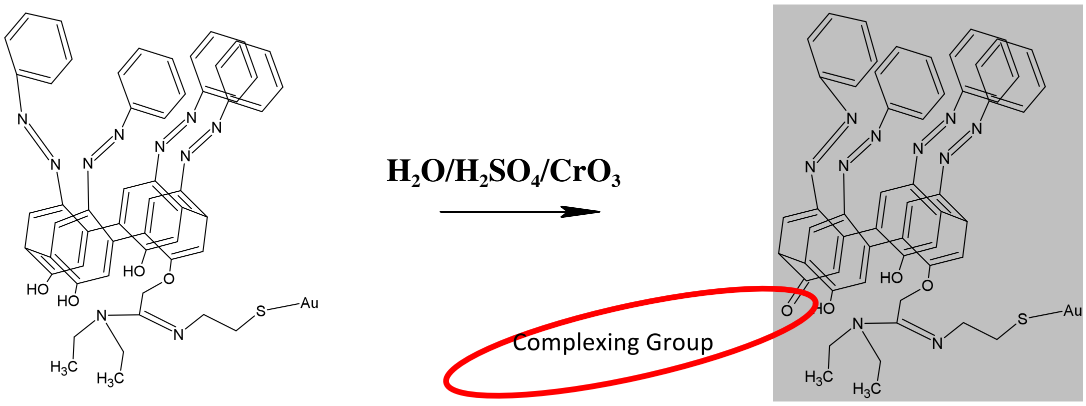


3. Cleaning of SAM by ethanol.
4. Deposition of calix[4]arene onto the SAM by spin coating method: An oxygen donor group of calixarene reacts with amine of SAM (Shervedani and

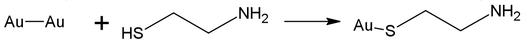
Mozaffari, 2005; Sunet al., 1998; Xia et al., 1999; Delvaux and Demoustier-Champagne, 2003):



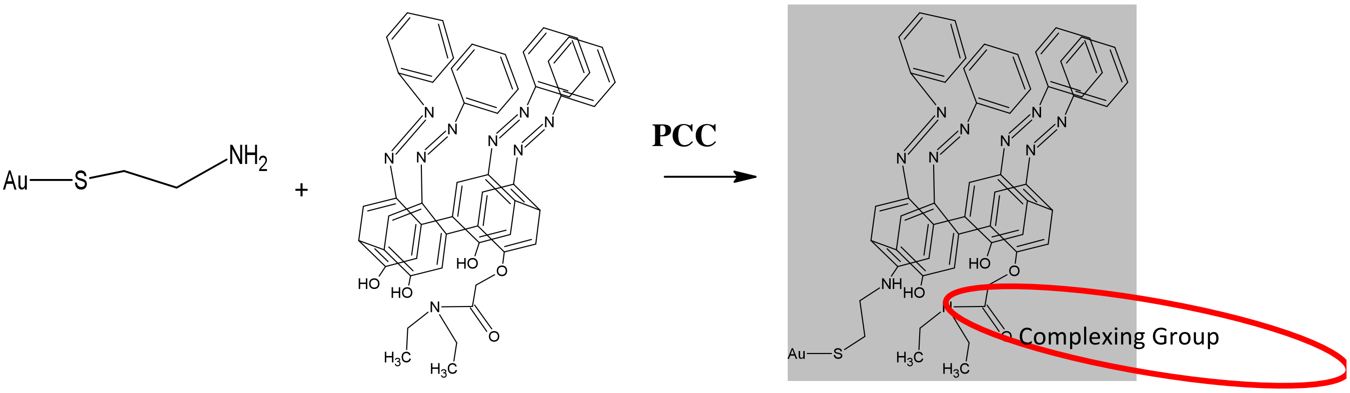
5. Activation of grafted surface by oxidation Cr_2O_3/H_2SO_4 in diluted water solution and formation of quinone (Hudlicky, 1990):



Second procedure steps:

1. In SPR the adhesion between the gold layer and glass is only physical. Pirhana was not made to clean the gold surface. Accordingly, acetone and ethanol were used,
2. Grafting of SAM on the gold surface: The sensor is plunged in 15mM of cysteamine solution for two hours: 

3. Cleaning of SAM with ethanol.
4. Deposition of calix[4]arene onto the SAM in PCC solution. PCC was made to protect the oxygen donor group and catalyze the reaction between SAM and calixarene alcohol group (Hunsen, 2005; Hunsen, 2005; Muzart, 1992).



3. RESULTS AND DISCUSSION

The sensor was characterized by electrochemical impedance spectroscopy EIS. All tests were made by SPR method. The influence of pH on ions detection was studied and optimized for each ion. The regeneration of the sensor was made by injection of 10mM EDTA.

3.1 Sensor characterisation by electrochemical impedance spectroscopy EIS

The EIS is a powerful technique for characterization and studying electrical and electrochemical properties of a large variety of systems.

All electrochemical measurements were carried out using VOLTALAB 40 analyzer (PGZ301 & VoltaMaster 4).

A three-electrode electrochemical cell was used with a chemical gold-electrode as the working electrode. A calomel-electrode was used as the reference electrode and a platinum-electrode was used as the auxiliary electrode. Measurements were used in buffer solution at adjusted pH of about 7.3.

Concerning the use of EIS to characterize thin films in contact with electrolyte solutions, three different contributions, bulk, interfacial and electrolytes may be determined (Macdonald, 1987). From an electrochemical point of view, when a metal is placed in contact with an electrolyte, a potential is generated due to the unequal distribution of charge across the interface. In addition, hydrated ions will not be able to approach indefinitely close to the interface. To explain such phenomena, Helmholts has proposed the well-known theory of the double layer. This interface behaves as widely described by Randles' equivalent circuit, (Fig. 4) (Macdonald, 1987; Hsu and Mansfeld, 2001; Ding et al., 2005). In such a model, the charge transfer resistance R1 is generally in parallel with the constant phase element CPE contained in the modified layer capacitance and the double layer capacitance and in series with the solution resistance Rs.:

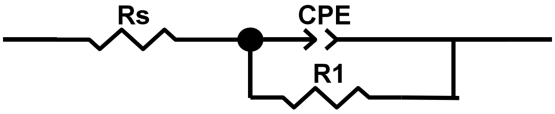


Figure 4 Equivalent circuit model, Rs, R1 and CPE represent the resistance of electrolyte, the charge transfer resistance, and constant phase element, respectively.

The EIS measurements were used to characterize the functionalized electrode. Fig. 5 shows the faradaic impedance spectra presented as Nyquist plots (Zim vs. Zre) upon the assembly of the three layers on the electrode:

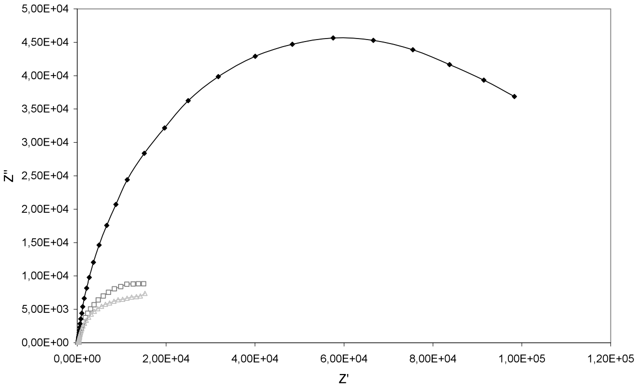


Figure 5 EIS measurement of sensor in buffer solution:

a) —△— Gold b) —□— SAM c) —■— Calixa[4]rene-SAM

The bare Au electrode exhibits an almost straight line (curve a) that is characteristic for a mass diffusional limiting electron-transfer process. In the case of gold electron-transfer, the resistance is about 8869Ω. Assembly of the cysteamine monolayer on the electrode surface (curve b) generates a layer on the electrode that introduces a barrier to the interfacial electron-transfer. This is reflected by the appearance of the semicircle part on the spectrum, corresponding to a charge transfer resistance of R1=24613Ω. The deposition of calix[4]arene onto the SAM cysteamine layer results in an increase of the electron-transfer resistance to R1=60052Ω (curve c). The covalent attachment of each layer increases the charge transfer resistance.

3.2 pH Optimization

The SPR method was used for pH optimization and test-sensors.

PH detection of the sensor was optimized for each ion at 1μM concentration. The pH of buffer solution was adjusted by using 0.1M of HCl or NaOH solution. Fig. 6 shows that ion detection is made in basic solution at a pH range between 7 and 8 (7.3 for copper, 7.8 for Cd^{+2} and Mg^{+2}, and 8 for cadmium). This is in agreement with proton/ion exchange (Norlin et al., 2002; Profumo et al., 2006). At low pH, quinone protonated and ion complexation does not take place. At pH>7, oxygen was deprotenated making the sensor surface become negatively charged. Thus, the incorporation of ion by the calix[4]arene-SAM can also be favored by electrostatic interactions (Freire and Kubota, 2004). Such coupling of favorable characteristics is most likely the key to achieving the remarkable sensitivity to ions of the proposed sensor.

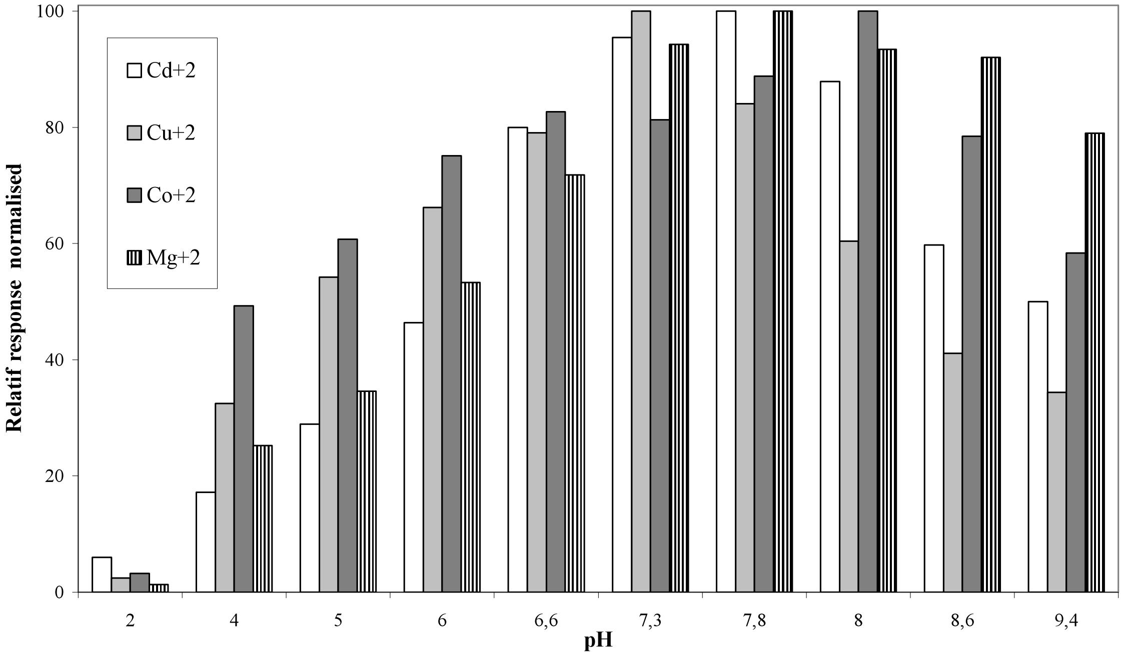


Figure 6 Optimization of pH for each ion.

3.3 Sensor detection

For all ions, we observed that the output refractive index increases with increasing ion concentration. As shown in (Halouani et al., 2002) metal ions are coordinated with the oxygen atoms of the amide group and complexation of ions takes place.

For the oxidation procedure, the detection limit reached is lower than 10^{-5} µM for the most heavy metals used. Detection limits reached are 2 10^{-6} µM, 3 10^{-6} µM, 4 10^{-6} µM, and 6 10^{-6} µM for Cu^{+2}, Co+2, Cd^{+2}, and Mg+ ions, respectively (Fig. 7):

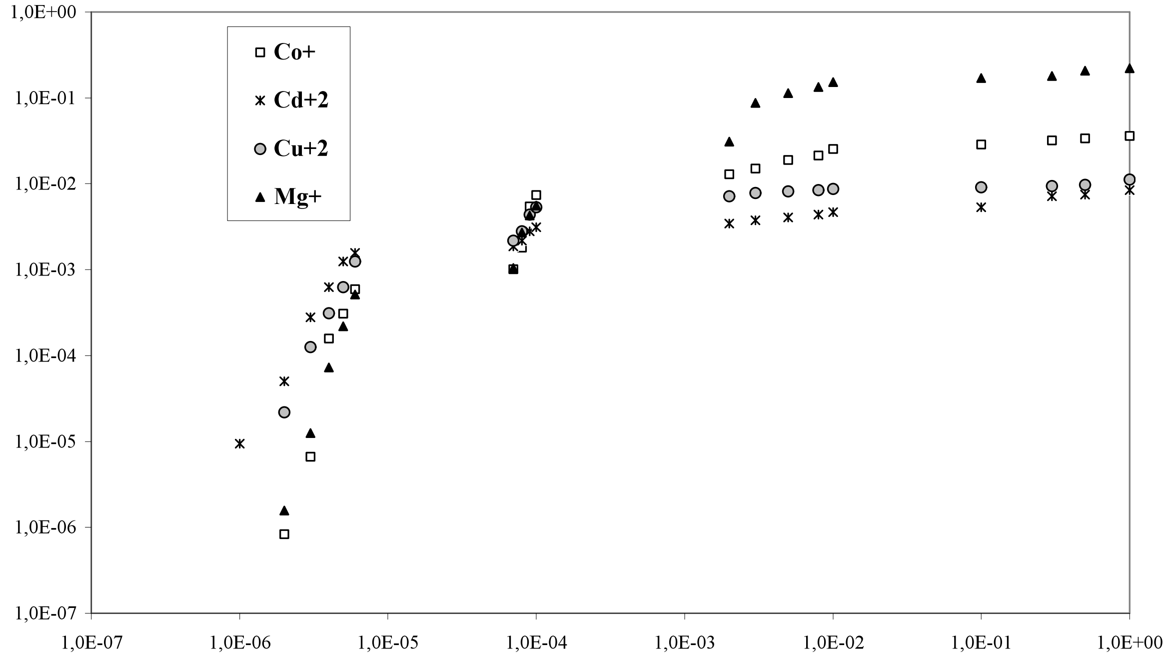


Figure 7 Calibration curve of SPR calix[4]arene SAM sensor for different zones of heavy metals detection: Oxidation procedure.

Four zones of detection were observed between 0 and 1µM.: A high concentration zone from 0.1 to 1µM (Fig. 8a), a second zone between 10^{-3} and 10^{-2} µM (Fig. 8b), a third zone between 10^{-4} and 10^{-5} µM (Fig. 8c) and a low concentration zone from 10^{-5} to 10^{-6} µM (Fig. 8d). In Figures 8a), b), c), and d), a linear variation of signal was showed for each heavy metal in all detection zones. The slopes of lines represent sensor-sensitivities. A recapitulative table which gives sensor-sensitivity for each zone was drawn (Tab. 1). As low sensitivities as 5.9 10^{-2}, 7.6 10^{-3}, 2.5 10^{-3} and 3.1 10^{-3} µM^{-1} for Mg^{+2}, Co^{+2}, Cu^{+2} and Cd^{+2} in high concentration zones respectively were observed. In the range between 10^{-4} and 10^{-5} µM, high sensitivity values were observed for heavy metals detection in which detection limit borders were reached. As shown in Tab. 1, the sensitivities obtained are 151.46, 210, 103.99, and 43.75µM^{-1} for Mg^{+2}, Co^{+2}, Cu^{+2} and Cd^{+2}, respectively:

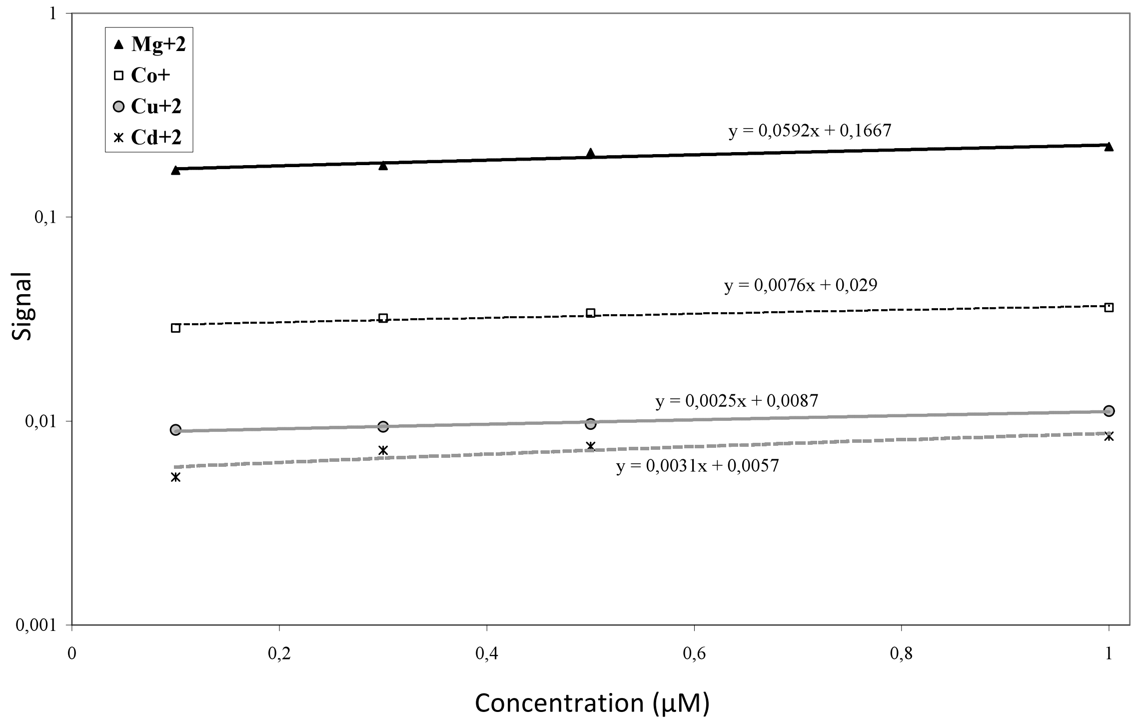


Figure 8 a) Behaviour of heavy metals adsorption on calixarene-SAM in different zones of detection Zone 1

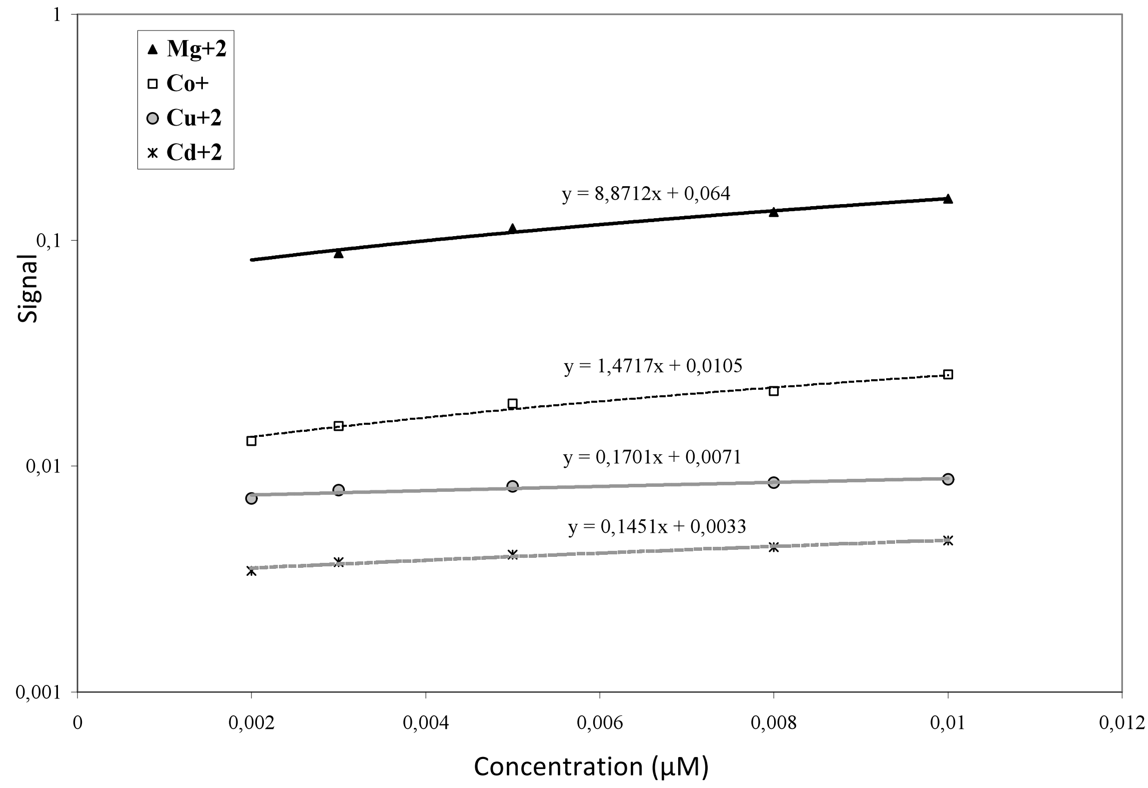


Figure 8 b) Zone 2

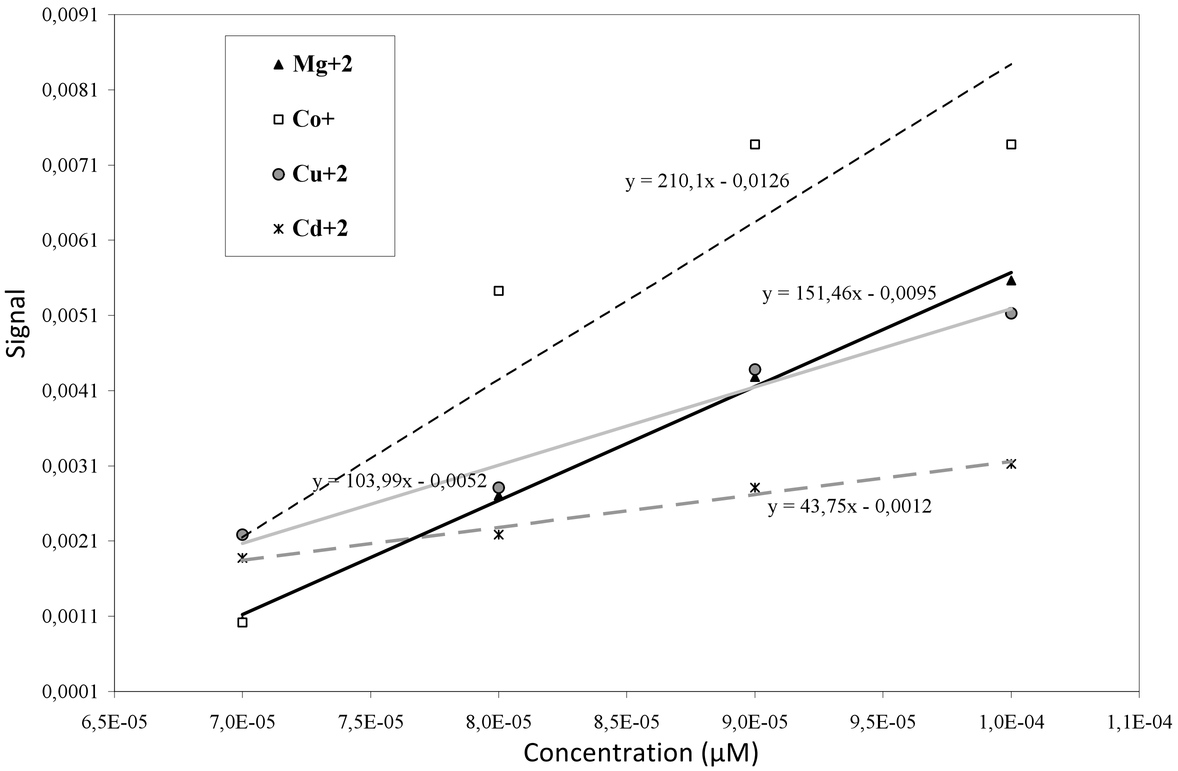


Figure 8 c) Zone 3

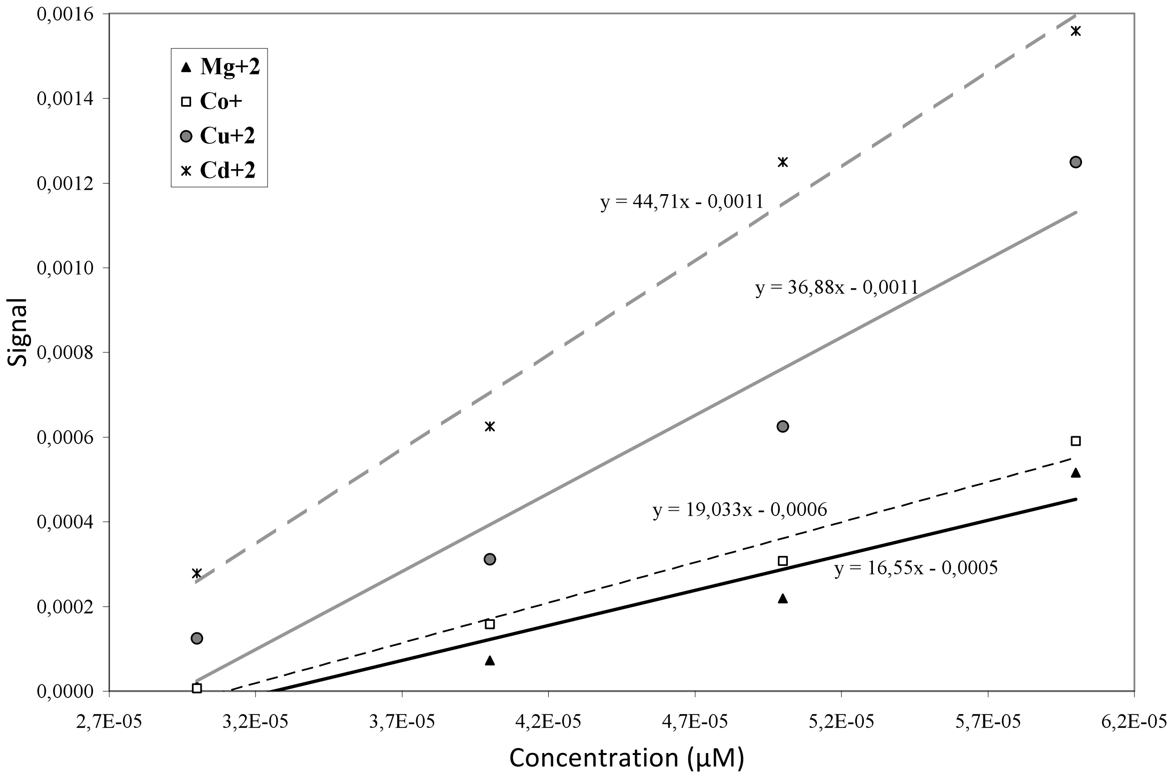


Figure 8 d) Zone 4

	Sensitivity (µM^{-1})			
	ZONE 1	**ZONE 2**	**ZONE 3**	**ZONE 4**
Mg^{+2}	0.0592	8,870	151,46	16,55
Co^{+2}	0.0076	1,470	210	19,033
Cu^{+2}	0.0025	0,170	103,99	36,88
Cd^{+2}	0.0031	0,145	43,75	44,71

Table 1 Sensor-sensitivities for the different zones: Oxidation procedure

In case of the second functionalization procedure where pyridine was made to protect oxygen donor group of calixarene (Fig. 9), copper and cadmium are only detected between 0 and 1µM. The detection-limit reached for Cd^{+2} is at about 10^{-5} µM and does not exceed 10^{-4} µM for copper. To determine the sensor-sensitivity, linear smoothing curves were plotted for each zone-detection. The same behavior was observed previously and a linear variation of a signal was shown for each heavy-metal in all detection-zones. Results obtained in Tab. 2 show different sensitivities of sensors for copper. The values obtained are 0.0024, 0.038, and 47.42µM^{-1} in the first, second, and third detection-zone, respectively. In case of the Cd^{+2} ion, the sensitivity values obtained are 0.0047, 0.60 to 4.12 and 20.42µM^{-1} for high concentration, second, third, and low concentration-zone, respectively.

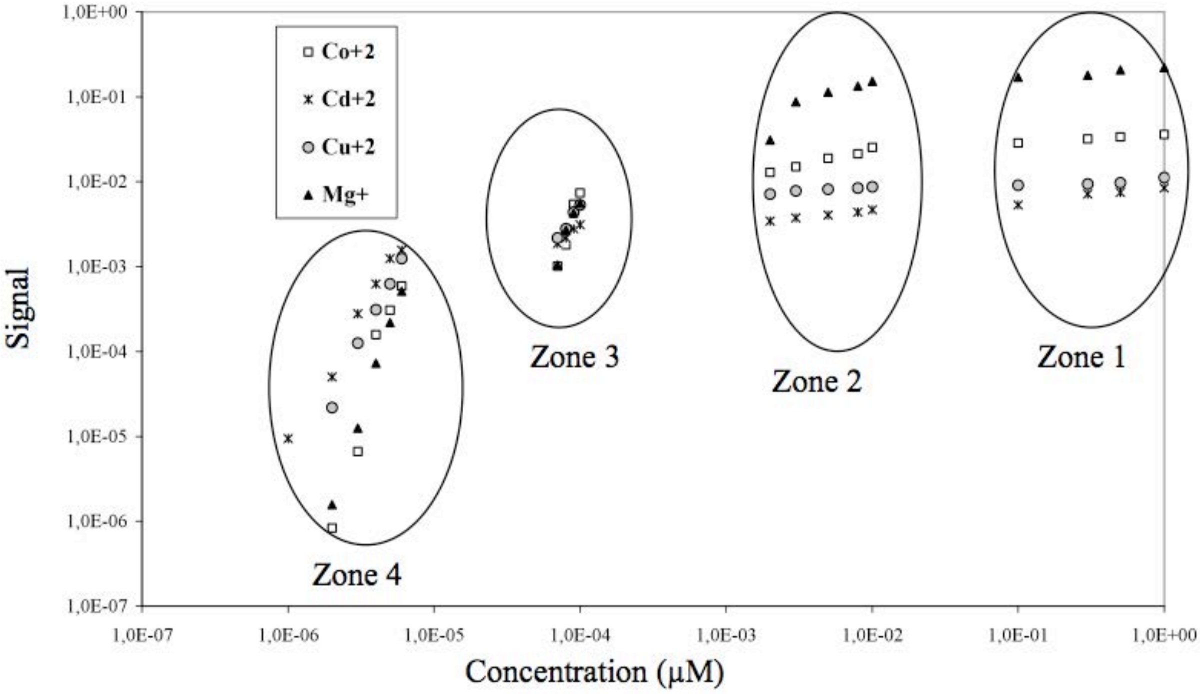


Figure 9 Calibration curve of SPR calix[4]arene SAM sensor for different zones of heavy metals detection: Second functionalization procedure

	Sensitivity (µM^{-1})			
	ZONE 1	**ZONE 2**	**ZONE 3**	**ZONE 4**
Cu^{+2}	0,0024	0,038	47,42	-
Cd^{+2}	0,0047	0,606	4,13	20,42

Table 1 Sensor-sensitivities for the different zones: Second procedure

Comparative results show that the second functionalization procedure is not adequate for heavy-metal detection and that the oxidation procedure is better, hence preferable for these types of ions.

We showed that signal is proportional to the capacity of adsorbed ions on the sensor-surface, which is in agreement with literature (Parsons et al., 1995; Karlsson, and Falt, 1997; Paarmann et al., 2002).

Different detection-limits observed for various heavy metals can be explained by several parameters: Adsorption potential and formation of various metal hydroxides which are not the same for different heavy-metals ion and oxygen deprotenation charging the sensor surface negatively (Halouani et al., 2002; Ma et al., 2001; Muñoz and Palmero, 2004; Farghaly, 2003). Accordingly, the incorporation of ions by the calix[4]arene-SAM can be favored by electrostatic interactions which directly influence the stability of complexes formed as well as its association binding (Freire and Kubota, 2004: Tsukube et al., 1997). Although there is an ionic force in aqueous media and interactions between host and guest such as π-stacking, dipolar-dipolar interactions have a strong influence on the stability of the complexes (Tsukube et al., 1997; Gong et al., 1998; Gocmen and Cakil, 1993; Rounaghi et al., 1997; Schneider, 1996; Bonas et al., 1998).

4. CONCLUSION

We demonstrated the possibility to use a new functionalized chromgenic calix[4]arene molecule onto SAM of cysteamine for the determination of ions in real samples. Such coupling of favorable characteristics is most likely the key to achieving the remarkable sensitivity to ions of the proposed sensors. We showed that ion detection depends on functionalized procedures and the pH of the solution. This work opens the way to sensors for selective ion detection and to the use of calix[4]arene in the field of biochemistry.

ACKNOWLEDGEMENT

This work was partly supported through laboratories of AMPERE, Ecole Centrale de Lyon (France) and LSA – Université Claude Bernard Lyon 1 (France).

REFERENCES

Aizenberg J., Black A.J., Whitesides G.M. (1998). Nature:394-868

Antesberger J., Cave G.W., Ferrarelli M.C., Heaven M.W., Raston C.L., Atwood J.L. (2005). Chemical Communications (Cambridge, England) (7):892-4

Arrigan D.W.M., Bihan L.L. (1999). Analyst 124:1645

Atwood J.L., Barbour L.J., Jerga A. (2002). Proceedings of the National Academy of Sciences 99 (8):4837-41

Barhoumi H., Maaref A., Mlika R., Martelet C., Jaffrezic-Renault N., Ponsonnet L. (2005). Materials Science and Engineering: C, Volume 25, Issue 1:61-66

Bonas G., Bosso C., Vignon M.R., Rapid Commun. Mass Spectrom., 2 (1988) 88

Bouazizi A., Maaref H., Jaffrezic-Renault N., Ben Chaabane R., Gammoudi M., Guillaud G., Sensors and Actuators B: Chemical, Volume 34, Issues 1-3, August 1996:487-489

Boussaad S., Pean J., Tao N.J. (2000). Anal. Chem. 72:222

Chah S., Fendler J.H., Yi J. (2002). Chem. Commun. 2094

Chen L., Zeng X., Ju H., He X., Zhang Z.I. (2000). Microchemical Journal, Volume 65, Issue 2:129-135

Corey E.J., Suggs J.W. (1975). Tetrahedron Letters, Volume 16, Issue 31:2647-2650

D. Sarkar, P. Somasundaran, J. (2003). Colloid Interface Sci. 261:197

David G. C. (1989). Cambridge: Royal Society of Chemistry, 1989

Delvaux M. and Demoustier-Champagne S. (2003). Biosens. Bioelectron. 18:943

Ding S.J., Chang B.W., Wu C. C., Lai M. F., Chang H.C. (2005). Analytica Chimica Acta, Volume 554, Issues 1-2, 4 December:43-51

Duncan D. M. and Cockayne J. S., Sensors and Actuators B: Chemical, Volume 73, Issues 2-3, 10 March 2001:228-235

Farghaly O. A. (2003). Microchemical Journal, Volume 75, Issue 2, September:119-13

Faull J. D., Gupta V.K. (2003). Thin Solid Films 440:129–137

Flink S., Boukamp B.A., van den Berg A., Fvan Veggel.C., Reinhoudt D.N., J. (1998). Am. Chem. Soc. 120:4652

Freire R.S., Kubota L. T. (2004). Electrochimica Acta 49:3795–3800

Gao Z.Q., Siow K.S. (1996) J. Electroanal. Chem. 412-179

Georgiadis R., Peterlinz K.P., Peterson A.W. (2000). J. Am. Chem. Soc. 122:3166

Gocmen A. (1993). Cakil, Anal. Chem., 342-471

Gong, C., Balanda, P. B., Gibson, H. W. (1998). Macromolecules, 31, 5278

Halouani H., Dumazet-Bonnamour I., Lamartine R. (2002). Tetrahedron Letters, Volume 43, Issue 21:3785-3788

Hsu C. S., Mansfeld F. (2001). Corrosion, 57, 747

Hudlicky M. (1990). ACS Monograph 186; American Chemical Society: Washington DC, Academic: New York

Jain A.K., Gupta Singh V.K., Srivastava L.P., Raisoni P., Talanta J.R. (2005). Volume 65, Issue 3:716-721

Karlsson, R. and Falt, A. (1997). J. Immunol. Methods 200, 121–133

Kumar S., Paul D., Singh H. (2006). Arkivoc 05-1699LU: 17 - 25. PMID

Levit N., Pestov D., Tepper G., Sensors and Actuators B: Chemical, Volume 82, Issues 2-3, 28 February 2002:241-249

Lu J., Chen R., He X. (2002). Journal of Electroanalytical Chemistry, Volume 528, Issues 1-2:33-38

Lu J.Q., Pang D.W., Zeng X. S., He X.W. (2004). Journal of Electroanalytical Chemistry, Volume 568:37-43

Ma Q., Ma H., Su M., Wang Z., Nie L., Liang S. (2001). Analytica Chimica Acta, Volume 439, Issue 1:73-79

Macdonald, J. R., ed., John Wiley, 1987, sect. 2.2.3.4

Mandler D., Turyan I. (1996). Electroanalysis 8:207

Mashazi P. N., Ozoemena1 K. I., Maree D.M., Nyokong T., Electrochimica Acta, In Press

McMahon G., O'Malley S., Nolan K., Diamond D., Arkivoc Part (vii), (2003)

Mo Hunsen (2005). Tetrahedron Letters, Volume 126, Issues 9-10:1356-1360

Mo Hunsen. (2005). Tetrahedron Letters, Volume 46, Issue 10, 7

Muñoz E. and Palmero S. (2004). Food Control, Volume 15, Issue 8:635-641

Muzart J. (1992). Chem. Rev. 92:113–140

Nachtigall F.F., Lazzarotto M., Braz F.N.J. (2002). Journal of the Brazillian Chemical Society 13 (3)

Norlin A., Pan J., Leygraf C. (2002). Biomolecular Engineering, Volume 19, Issues 2-6:67-71

Paarmann I., Spangenberg O., Lavie A., Konrad M. (2002). The journal of biological chemistry vol. 277, No. 43, Issue of October 25:40832–40838

Park J., Groves W.A., Zellers E.T. 1999). Anal. Chem., 71/17:3877–3886

Park J., Sun K. Kang, Chung T. D., Chang S.K., Kim H. (2001). Microchemical Journal, Volume 68, Issues 2-3, March:109-113

Parsons I. D., Perssoni B., Mekhalfia A., Michael Blackburn G., Peter Stockley G. (1995). Nucleic Acids Research, Vol. 23, No. 2

Pérez-Jiménez C., Escriche L., Casabó J. (1998). Analytica Chimica Acta, Volume 371, Issues 2-3:155-162

Profumo A., Merli D., Pesavento M. (2006). Analytica Chimica Acta, Volume 557, Issues 1-2, 31 January:45-51

Purse B.W., Gissot A., JRebek. Jr. (2005). Journal of the American Chemical Society 127 (32):11222-3

Rounaghi G., Eshaghi Z., Ghiamati E. (1997). Talanta, 44:275

Sato Y., Fujita M., Mizutani F., Uosaki K., J. (1996). Electroanal. Chem. 409-145

Schneider J. Org. Chem., 61 (1996) 5221

Shervedani R. K. and Mozaffari S.A. (2005). Surface and Coatings Technology, Volume 198, Issues 1-3:123-128

Steinberg S., Rubinstein I. (1992). Langmuir 8 1183

Sun J., Fang H.-Q., Chen H.-Y. (1998). Analyst 123:1365

Thallapally P.K., Lloyd G.O., Atwood J.L., Barbour L.J. (2005). Angewandte Chemie (International ed. in English) 44 (25):3848-5

Tsukube, H., Furuta, H., Odani, A., Takeda, Y., Kudo, Y., Inoue, Y., Liu, Y., Sakamoto, H., Kimura, K. (1997). Compreshensive Supramolecular Chemistry; Davies, J. E. D.; Ripmeester, J. A., Eds. Pergamon: Oxford, UK, Vol. 8:425

Ulman A., in: An Introduction to Ultrathin Organic Films, Academic Press, Boston, 1991

Xiao Y., Ju H.-X., Chen H.-Y. (1999). Anal. Chim. Acta 391:73

Zacher T., Wischerhoff E. (2002). Langmuir 18:1748