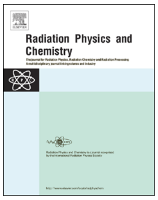
Radiation Physics and Chemistry 94 (2014) 133–136

Contents lists available at ScienceDirect

Radiation Physics and Chemistry

journal homepage: www.elsevier.com/locate/radphyschem



Radiation-grafted, chemically modified membranes part I – Synthesis of a selective aluminum material

Renata Bazante-Yamaguishi, Eduardo Moura, José E. Manzoli, Aurea B.C. Geraldo*

Nuclear and Energy Research Institute (Instituto de Pesquisas Energéticas e Nucleares), IPEN–CNEN, SP, Av. Prof. Lineu Prestes, 2.242 Cidade Universitária, 05508-000 São Paulo SP, Brazil

HIGHLIGHTS

- Chemical modification of styrene grafted PP and PVC membranes by irradiation process.
- PP samples achieved the chemical modification and conserved their membrane shape.
- Alternative reactions were applied to obtain the final product.

ARTICLE INFO

Article history:
Received 10 January 2013
Accepted 10 June 2013
Available online 27 June 2013

Keywords:
Styrene grafting
Polypropylene
Poly(vinyl chloride)
Selective membrane
Aluminum

ABSTRACT

Polymeric membranes were styrene grafted by irradiation methods and the obtained material was chemically modified to become aluminum selective. For this purpose, polymeric substrates of PVC (polyvinyl chloride) and PP (polypropylene) were styrene grafted mutually by gamma and electron beam irradiation. The modification process includes three basic reaction paths: Friedel–Crafts acylation, 2-methylanisole coupling and a final oxidation to achieve aluminum selectivity. Although this specific chemical modification in derivatives of polystyrene is not new, the new challenge is to obtain a selective material where original membrane characteristics (physical shape and mechanical resistance) are minimally conserved after such an aggressive treatment.

1. Introduction

In the research of quality management of water resources, special attention has been historically dedicated to heavy metals (Cr, Hg, Pb) because their presence is associated to short-term environmental and human health disturbances; however, aluminum flocculants are also used as particle removers at water treatment stations. Thus, in the last decades the study of aluminum ions in water gained high importance because of chronical diseases associated to their presence, such as cerebral sclerosis (Alzheimer and Parkinson diseases) and osteoporosis (Tomljenovic, 2011) which are generally developed by high level aluminum absorption into human body; also, random disturbances like irritability and seborrhea are linked to aluminum concentration above maximum contaminant level (viny), which amounts up to the maximum of 200 ppb in European and Brazilian regulations and 50–200 ppb for US-EPA regulations.

Aluminum appears in most of both the natural and the processed human consumption sources; thus, it is mandatory to determine quantitatively its presence, in order to take remediation decisions. Aluminum concentration can be determined by simple methods such as titration and spectrophotometry, respecting the detection limits of each method and type of interfering species. A classical spectrophotometric method is to obtain an aluminum colored complex by alizarin and its conformational analogous, where the aluminum atom is chelated by 1-hydroxy and 9-carboxyl group of alizarin's aromatic ring. The complex Al-alizarin is quickly formed and it remains stable for hours; these characteristics allow its use on this analytical method (Pobiner, 1961).

The use of metal ion collectors prior analytical determination by AAS, ICP-AES or IC methods is required when trace level metal analysis is required (Motellier and Pitsch, 1994; Tangen et al., 2002; Khan et al., 2009). Modified resins and other adsorbent materials provide physical support to immobilize specific substances, which may contain also specific functional groups that may provide high selectivity to bind to specific chemical species. In the case of aluminum, many substances are used for this purpose: tiron (1,2-dihydroxy-3,5-benzenedisulfonic acid) (Luo and Bi, 2003),

---

* Corresponding author.
E-mail addresses: jmanzoli@ipen.br (J.E. Manzoli), ageraldo@ipen.br, aureabeatriz.cerqueirageraldo@gmail.com (A.B.C. Geraldo).

0969-806X/$ - see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.radphyschem.2013.06.008

pyrocathecol violet (Tria et al., 2008), 8-hydroxyquinoline-5-sulfonic acid – HQS (Carnevale and Jackson, 1994; Luo et al., 2004), Eriochrome Cyanine R, Solochrome Violet, Xylenol orange, Ferron, and Alizarin Red S (Luo et al., 2008). Such compounds have at least one set of side hydroxyl groups, hydroxyl near ketone groups or oxygen from sulfonic groups near ketone and/or hydroxyl groups, and all of these are classical molecular arrangements for aluminum chelation. Aluminum then binds strongly to groups with high donor tendency, such as negatively charged oxygen, and thus complexes are formed.

Despite the availability of these substances, aluminum complexes with salicylic acid and its derivatives also have high equilibrium constants (Martell et al., 1990) and under low to medium pH, their sorption capacity is high compared to calcon, HQS and tiron (Kiss et al., 1993) which also have high aluminum sorption capacities. Salicylic acid and its derivatives have a simpler molecular arrangement and their synthesis in solid supports is not complex (Tewari and Singh, 2000; Boudenne et al., 2002); in such cases, poly(styrene-*co*-divinylbenzene) resins like Amberlite XAD-2 and XAD-4 had been salicylate supported from classical organic reactions.

In this work, salicylated membranes are synthesized from styrene grafting on polymer supports by ionizing irradiation, with inexpensive polypropylene (PP) and polyvinyl chloride (PVC) as the chosen polymer substrates. The challenge was to produce an aluminum selective material based on irradiated, styrene grafted membranes that keep their initial physical aggregation conditions even after being submitted to a very aggressive set of organic reactions. These two kinds of polymeric substrates and its distinct degrees of grafting were needed to apply the chemical modification and evaluate their results.

2. Experimental

The polymer substrates undertook two kinds of processes: irradiation (styrene grafting, Moura et al., 2011,Moura et al., 2012) and chemical (production of a salicylic acid derivative). PVC samples could not stand the final reaction of the first step of chemical modification (chlorination with thionyl chloride) and the resulting product was a shapeless material. On the other hand, PP samples endured the complete treatment, providing samples which were suitable for analysis.

Styrene grafting on polymer substrates by ionizing radiation process: Goodfellow's PP samples with thickness of 0.10 mm and PVC samples of commercial film (Vulcan) with thickness of 0.21 mm were acquired. Polymer samples of 40 (W) × 40 (L) mm were washed in analytical grade ethanol and dried at room temperature. The chosen monomer was commercial grade styrene, pretreated by inhibitor removal with molecular sieves. The grafting media were 1:1 and 1:3 styrene/solvent mixtures, where analytical grade *n*-butanol and *n*-octanol were applied.

The mutual irradiation grafting was performed using two sources:

- Job 188 Dynamitron® Electron Beam Accelerator with 1.5 MeV energy, with beam current of 25 mA, beam power of 37.5 kW and scan range from 50 to 120 cm, where irradiation conditions comprised doses of 50 kGy and dose rate of 2.2 kGy/s (only PP samples).
- ^{60}Co source from Gamma Cell M-220, where irradiation process was performed at 50 kGy of absorbed dose and 1.50 Gy/h of dose rate.

All samples were homo-polymer extracted by toluene immersion (2 days), followed by several cycles of ethanol washing and finally vacuum drying at 50 °C. The styrene grafted samples were analyzed by gravimetry to determinate the grafting yield; the final values have been averaged from a series of three measurements.

Production of salicylic acid derivative on styrene grafted membranes by organic chemical process: this process comprised three basic sets of chemical processes: Friedel–Crafts acylation, 2-methylanisole coupling plus final oxidation and O-demethylation, this last step providing the aluminum selectivity.

In the first step, the polymer samples were acetylated following the method described by Sarvari and Sharghi (2004), where reaction occurs with acetylchloride (reagent and solvent in the same time) and a 2 mmol zinc oxide solution at room temperature for 5 minutes. After this reaction, the polymer samples were washed with 1:1 hydrochloric acid aqueous solution, followed by further washing with water and methanol. The acetylated samples were then oxidized by $KMnO_4$ (15 mmol) and NaOH (0.14 mmol) aqueous solutions at room temperature during 4 h. Next, the oxidized samples were washed again several times with deionized water and then flushed with thionyl chloride at 60 °C for 15 min with stirring. These final oxidation and chlorination reactions were based on the method described by Boudenne et al. (2002).

The 2-methylanisole coupling is actually a different Friedel–Crafts acylation, where one pours now this said reagent (which was also the reaction solvent, as in the first step) onto a 2 mmol zinc oxide solution in order to perform the reaction at room temperature for 10 min with intermittent stirring. The samples were washed several times with deionized water and methanol. A new oxidation with $KMnO_4$ with the same solution, temperature and time as in the first step was performed. Next, after even more washes with deionized water, the MnO_2 residue formed by this oxidation reaction was then removed from the samples by immersing them in an 1:1 HCl aqueous solution and with a final washing cycle with deionized water and methanol.

Finally, the last step was based on the method described by Kende et al. (1976), where dried samples were immersed in toluene and 2 mmol anhydrous aluminum chloride mixture at room temperature overnight with stirring. After this reaction, the samples where immersed in an 1:1 HCl aqueous solution and washed several times with deionized water and methanol; the dried final product had a light brown color.

The reaction molar yield was determined by gravimetry for each step. The reaction steps were qualitatively monitored by Mid-ATR-FTIR, performed on a Perkin-Elmer FTIR spectrophotometer model spectrum 100.

3. Results and discussion

Table A1 shows the degree of grafting of the samples. The results are dependent on the type of polymer, irradiation method and composition of the grafting media. Gamma irradiation promotes high yields of grafting due the very low dose rate of the used source. Besides the quantitative characterization of these samples, an important remark is their visual aspect: low degree of grafting results in flat and smooth samples; the increase of the degree of grafing promotes a wrinkled final product.

For the chemical modification process, the first step is the most important, since its resulting yield impacts directly both qualitative and quantitative selectivity of the membrane as a final product. Conversely, this yield depends on the access of the catalyst and acylation reagent to the sample. When the reaction is performed with a ZnO concentration under 2 mmol, the reaction yield is low (about 8.7% for grafted PVC and 9% for grafted PP). Values between 3 and 5 mmol of this catalyst yield more than 85% of acylation for grafted PVC and about 20% for grafted PP. PVC swelled significatively during the reaction process, suggesting that the swelling may increase the accessibility of acylation reagent throughout the sample. Thus, two pre-treatments were applied to grafted PP samples in order to increase its reaction yield.

Table A1
Styrene grafting on polymer substrates by mutual ionizing radiation process. Values show the average of three measurements with standard deviation in brackets.

Sample	Irradiation method	Grafting media	Degree of grafting (%)
PP-1	Gamma	Styrene:*n*-butanol 1:1	99 (4.2)
PP-2	Electron-beam	Styrene:*n*-octanol 1:1	33 (14)
PVC-1	Gamma	Styrene:*n*-butanol 1:1	61 (4.1)
PVC-2	Gamma	Styrene:*n*-octanol 1:3	21 (1.2)

Table A2
Grafting yields for each chemical modification step. Values show the average of three measurements with standard deviation in brackets.

Modification step	Conditions	Sample	Yield (%)
1st	ZnO as catalyst	PVC	8.7 (1.8)
	<2 mmol	PP	9.0 (1.8)
	ZnO as catalyst	PVC	85 (0.2)
	3 to 5 mmol	PP	20 (0.2)
	ZnO as catalyst 3–5 mmol Pre-immersed in toluene	PP	60 (0.2)
	ZnO as catalyst 3–5 mmol Pre-immersed in chloroform		84 (0.1)
	$KMnO_4$ + NaOH, 4 h	PVC	97 (1.6)
		PP	95 (1.6)
	$SOCl_2$, 70 °C, 15 min	PVC	Damaged
		PP	80.7 (16)
2nd	2-Methylanisole ZnO as catalyst 3–5 mmol	PP	80.7 (1.6)
	$KMnO_4$ + NaOH, 12 h		84 (0.1)
3rd	Toluene, $AlCl_3$		84 (0.1)

PP did not swell in acetylchloride; the samples were then pre-swelled with toluene and chloroform. The acylation reaction applied in the samples pre-immersed by 1 h in toluene resulted in yields around 60%; when the PP samples are pre-immersed in chloroform for the same time, the reaction yield increases to 84%. This result may be related to the molecular interaction characteristics between the swelling solvent and acetylchloride, which is simultaneously solvent and reagent: the acetylchloride interacts better into grafted PP swollen by chloroform due the polar nature of these both solvents, increasing the resulting yield toluene also promoted significative swelling as well, but its apolarity does not promote accessibility of the reagent to the bulk of PP samples, and the resulting yield is low.

For PP, it was found that high yields in the first step of chemical modification provide for high yields on the following steps, as shown in Table A2. PVC samples could not be evaluated, since they could not stand the third step of reaction with thionyl chloride, even when the samples are immersed for less than 5 min.

Fig. B1 shows the ATR-FTIR spectra of PP styrene grafted samples for all steps of modification. The first spectrum shows the initial substrate after gamma irradiation process; characteristic absorption bands of grafted styrene occur at 690 cm^{-1} (out-of-plane C–H bond vibrations of the aromatic ring), at 750 cm^{-1} (out-of-plane bending H atoms bonds in the aromatic ring), at 1491 cm^{-1} and 1595 cm^{-1} (plane deformation of C=C bonds of styrene backbone). The second spectrum is related to the first Friedel–Crafts reaction, where absorption bands at 1196 cm^{-1} and at 1260 cm^{-1} (arylketones) and at 1337 cm^{-1} (deformation vibration of CO–CH_3 bond) are present. The third spectrum shows the 2-methylanisole coupling reaction on polymeric substrate, with absorption bands at 1122 cm^{-1} (vibration of C–O bond at ethoxy group) and at 1015 cm^{-1} (deformation band of tri-substituted phenyl). The last spectrum shows the last step of chemical modification of polymer membrane samples, where the deprotection of the methoxy group caused the disappearing of the absorption band at 1122 cm^{-1}.

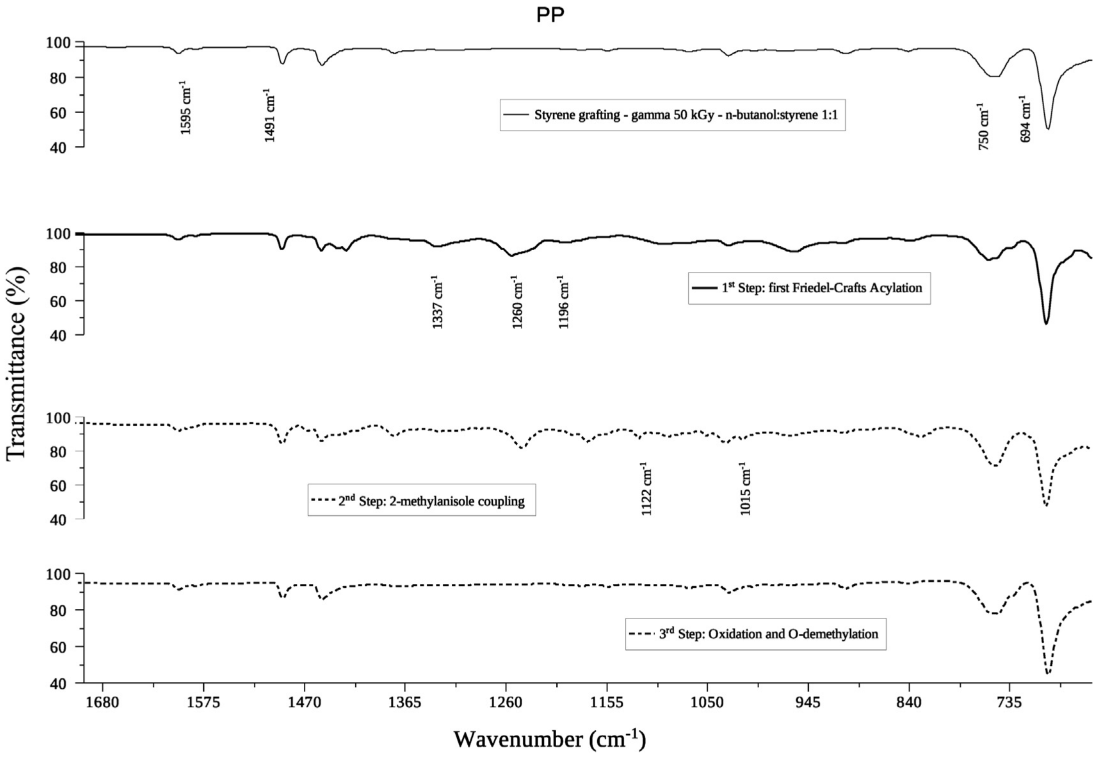


Fig. B1. ATR-FTIR spectra of PP styrene grafted samples for all steps of modification.

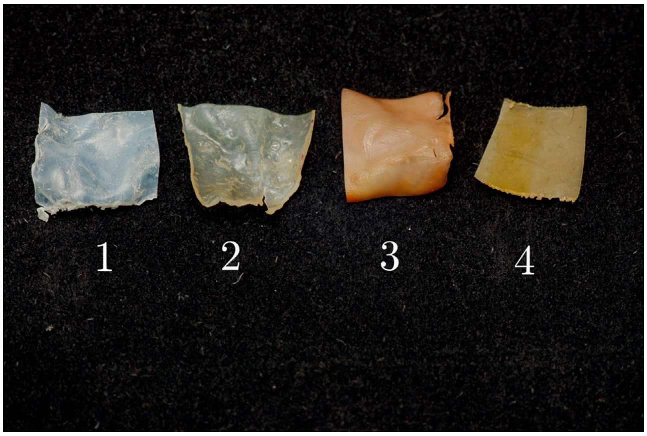


Fig. B2. Physical aspect of the final product. (1) Styrene grafted PP-1, with high yield of grafting (not chemically modified). (2) Chemically modified PP-1 (low yield – first step of modification). (3) Chemically modified PP-1 (high yields – first step of modification and grafting). (4) Chemically modified PP-2 (high yield for the first modification and low yield of grafting).

The chemical modification applied at polymer membrane samples is less aggressive than the modification made by Boudenne et al. (2002). The majority of reactions described in this paper were achieved at room temperatures and the utilization of organic solvents was minimized, since the polymer substrates were neither reinforced mechanically nor previously submitted to the cross-linking process. The final product based on PP matrix conserved its membrane shape; this is shown in Fig. B2(1)–(4). Initially the styrene grafted PP membrane obtained by ionizing radiation process presented a white translucent color (Fig. B2(1)); at the end of the chemical process, low yield in the first step of the chemical modification led to PP-1 which showed a light brown, translucent aspect (Fig. B2(2)); PP-1, with high yields of chemical modification and grafting (Fig. B2(3)) and PP-2, with high yield of chemical modification but with low degree of grafting (Fig. B2.4) presented opaque, light brown color as referenced above.

4. Conclusions

PP and PVC styrene grafted membranes by ionizing radiation process were chemically modified and this process comprised three basic steps: Friedel–Crafts acylation, 2-methylanisole coupling/final oxidation and O-demethylation (which provides the aluminum selective characteristic). Styrene grafted PVC membranes could not stand the aggressiveness of the first step of chemical process after irradiation process and the result was a desegregated mass. All tested PP samples achieved the chemical modification and conserved their membrane shape. Alternative and less aggressive reactions were then applied to obtain the final product.

Acknowledgments

The authors are grateful to financial support of FAPESP (São Paulo State Research Support Foundation – Brazil) through the process 2011/23426-8. We also thank Mr. Hiroshi Oikawa for Mid-ATR-FTIR spectroscopy; the work group of Accelerator facility at Radiation Technology Center (CTR) at IPEN-CNEN/SP, Ms. Elisabeth S.R. Somessari and her team (Mr. Carlos G. Silveira, Mr. Hélio A. Paes, and Mr. Carlos A. Souza); and Mr. Paulo A. G. Fessel for technical revision, support of the LaTeX/LyX typesetting system and for the picture of the membrane samples.

Appendix A

See Tables A1-A2.

Appendix B

See Figs. B1-B2.

References

Boudenne, J.-L., Boussetta, S., Brach-Papa, C., Branger, C., Margaillan, A., Théraulaz, F., 2002. Modification of poly(styrene-*co*-divinylbenzene) resin by grafting on an aluminium selective ligand. Polym. Int. 51 (10), 1050–1057 ⟨http://onlinelibrary.wiley.com/doi/10.1002/pi.918/abstract⟩.

Carnevale, J., Jackson, P., 1994. Analysis of aluminium in pharmaceutical products by post-column derivatization ion chromatography. J. Chromatogr. A 671 (June (1–2)), 115–120 ⟨http://www.sciencedirect.com/science/article/pii/0021967394802297⟩.

Kende, A.S., Tsay, Y.-G., Mills, J.E., 1976. Total synthesis of (.+-.)-daunomycinone and (.+-.)-carminomycinone. J. Am. Chem. Soc. 98 (March (7)), 1967–1969 ⟨http://dx.doi.org/10.1021/ja00423a056⟩.

Khan, S., Kazi, T.G., Baig, J.A., Kolachi, N.F., Afridi, H.I., Shah, A.Q., Kandhro, G.A., Kumar, S., 2009. Separation and preconcentration of trace amounts of aluminum ions in surface water samples using different analytical techniques. Talanta 80 (Nov 1), 158–162, PMID: 19782206.

Kiss, T., Atkári, K., Jezowska-bojczuk, M., Decock, P., 1993. Complexes of al(III) with hydroxyaromatic ligands. J. Coordination Chem. 29 (1–2), 81–96 ⟨http://www.tandfonline.com/doi/abs/10.1080/00958979308037128⟩.

Luo, M., Bi, S., 2003. Solid phase extraction-spectrophotometric determination of dissolved aluminum in soil extracts and ground waters. J. Inorg. Biochem. 97 (September (1)), 173–178 ⟨http://www.sciencedirect.com/science/article/pii/S0162013403002435⟩.

Luo, M., Bi, S., Wang, C., Huang, J., 2004. Determination of polymeric aluminum in soil extracted with a modified anion-exchange resin as a solid-phase adsorbent by ICP-AES. Anal. Sci.: Int. J. Jpn. Soc. Anal. Chem. 20 (January (1)), 95–100, PMID: 14753264.

Luo, M.-B., Wu, H., Zhang, J., Shen, D., Bi, S.-P., 2008. Determination of aluminum fractionation in soil extracts by using eriochrome cyanine r modified anion-exchange resin as solid phase extraction cartridge coupled with ICP-AES. Sep. Sci. Technol. 43 (8), 2225–2241 ⟨http://www.tandfonline.com/doi/abs/10.1080/01496390801940499⟩.

Martell, A.E., Motekaitis, R.J., Smith, R.M., 1990. Aluminium complexes of hydroxyaliphatic and hydroxyaromatic ligands in aqueous systems–some problems and solutions. Polyhedron 9 (2–3), 171–187 ⟨http://www.sciencedirect.com/science/article/pii/S0277538700805665⟩.

Motellier, S., Pitsch, H., 1994. Determination of aluminium and its fluoro complexes in natural waters by ion chromatography. J. Chromatogr. A 660 (February (1–2)), 211–217 ⟨http://www.sciencedirect.com/science/article/pii/0021967394851158⟩.

Moura, E., Manzoli, J., Geraldo, A., 2012. Effects of solvent polarity on mutual styrene grafting onto polypropylene by electron beam irradiation. Radiat. Phys. Chem. 81 (September 9), 1309–1313 ⟨http://www.sciencedirect.com/science/article/pii/S0969806X12000643⟩.

Moura, E., Somessari, E., Silveira, C., Paes, H., Souza, C., Fernandes, W., Manzoli, J., Geraldo, A., 2011. Influence of physical parameters on mutual polymer grafting by electron beam irradiation. Radiat. Phys. Chem. 80 (February (2)), 175–181 ⟨http://www.sciencedirect.com/science/article/pii/S0969806X1000318X⟩.

Pobiner, H., 1961. The aluminum-alizarin complex as a measure of Friedel–Crafts catalysts in paraffin hydrocarbon systems. Anal. Chem. 33 (May (6)), 790–793 ⟨http://dx.doi.org/10.1021/ac60174a038⟩.

Sarvari, M.H., Sharghi, H., 2004. Reactions on a solid surface. A simple, economical and efficient Friedel-Crafts acylation reaction over zinc oxide (ZnO) as a new catalyst. J. Org. Chem. 69 (October (20)), 6953–6956 ⟨http://dx.doi.org/10.1021/jo0494477⟩.

Tangen, G., Wickstrøm, T., Lierhagen, S., Vogt, R., Lund, W., 2002. Fractionation and determination of aluminum and iron in soil water samples using SPE cartridges and ICP-AES. Environ. Sci. Technol. 36 (December (24)), 5421–5425, PMID: 12521170.

Tewari, P.K., Singh, A.K., 2000. Thiosalicylic acid-immobilized amberlite XAD-2: metal sorption behaviour and applications in estimation of metal ions by flame atomic absorption spectrometry. The Analyst 125 (December (12)), 2350–2355, PMID: 11219081.

Tomljenovic, L., 2011. Aluminum and alzheimer's disease: after a century of controversy, is there a plausible link?. J. Alzheimer's Dis. 23 (4), 567–598, PMID: 21157018.

Tria, J., Haddad, P.R., Nesterenko, P.N., 2008. Determination of aluminium using high performance chelation ion chromatography. J. Sep. Sci. 31 (July (12)), 2231–-2238, PMID: 18563745.