Application of MnO₂Resin and Dowex 1X8 manganese dioxide impregnated resin for the separation of chromium from biological samples

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Abstract

MnO₂Resin and Dowex 1X8 manganese dioxide impregnated resin was used for chromium separation from biological samples. We examined sorption of chromium from acid solutions: hydrochloric, nitric and sulphuric in concentration range from 0.01 to 2 mol/dm³. The sorption process was evaluated by batch and column experiments. We also examined sorption of other elements in the developed systems, to check the selectivity of the process. Determination of chromium by radiochemical neutron activation analysis after separation with MnO₂Resin was described.

Keywords MnO₂Resin · Dowex 1X8 manganese dioxide impregnated resin · Chromium sorption · Radiochemical neutron activation analysis · Chromium determination

Introduction

Chromium is one of the elements widely distributed in the environment [1]. The large amounts of this metal come from industrial activities like electroplating, pigment production, leather tanning, and wood processing [2, 3]. The properties of chromium depend upon oxidation states and are very different. Chromium(III) is an important microelement, which is necessary to glucose, lipid and protein metabolism. Chromium(VI) has strong oxidizing potential and can easily penetrate biological membranes. The consequences of excessive exposure to this form may be skin damage, respiratory problems or in the same case cancer of kidneys, lungs or liver [4–7]. For these reasons amounts of this metal in biological and geological samples should be constantly monitored. Institutions like EPA, FAO/WHO and EU recommend the permissible content of chromium in water, food and soil [8–12].

Determination of chromium is often realized after separation process with the use of exchange resin. Ion exchange method gives the possibility to recover and concentrate elements of interest from samples with different matrices. This method has many advantages such as: easy recovery of the element, low operation cost, selectivity, concentration of the element of interest, removal of interfering ions and possible regeneration of the resin after processing [13, 14]. Many adsorbents are used for chromium preconcentration, e.g. Amberlite IRA-910 [15], Dowex 1X8 [16], Amberlite IRA-96 [16], activated carbon [17], functionalized Amberlite XAD-7 [18] and nanoparticles (TiO₂) [19].

MnO₂Resin is an inorganic, amphoteric resin dedicated for sorption of radium from water samples [20]. This resin is characterized by high surface area, oxidizing properties and stability under acidic conditions. MnO₂Resin was used primarily to extract radium from liquid waste by the uranium industry and to monitor marine waters for the presence of radioisotopes released from a nuclear reactor. The use of this sorbent is also mentioned in the literature for the preconcentration of lead, cadmium and chromium [21–23]. In natural systems (soils, water) manganese dioxide (MnO₂) is a strong oxidizing agent which oxidizes Cr(III) to Cr(VI). The oxidation process depends upon concentration of soluble Cr, pH, surface area and the form of MnO₂ [24]. Chromium(III) oxidation by MnO₂ has fast initial stage and then proceeds to the slower rate [25]. Chung et al. studied

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the oxidation process of Cr(III) by three different Mn oxides: hausmanite, binnite and pyrolusite. Generally hausmanite, which has the highest Mn content, is a better oxidizing agent than binnite or pyrolusite [26]. Moreover Cr(VI) is also sorbed on the MnO_2 surface. Bhutani et al. [27] reported that the chromate ions have a strong affinity for the surface of manganese dioxide and suggested the sorption process takes place by a mechanism of ligand exchange. Gheju et al. reported that the sorption process of Cr(VI) on MnO_2 can occur through two mechanisms: physical (non-specific adsorption, electrostatic interactions) and chemical (specific adsorption, chemical interactions). Non-specific adsorption by electrostatic interactions comes from the charge of the MnO_2 surface. The charge of the MnO_2 surface depends on the pH of the solutions, in acidic medium it is positively charged and in basic medium—negatively. Generally, the sorption of chromates or dichromates occurs rapidly from acidic solutions. Specific adsorption in the case of Cr(VI) takes place as a result of ionic sphere complexation [28].

In our previous paper we have developed a procedure based on radiochemical neutron activation analysis where the separation process of chromium was carried out using MnO_2 Resin. Application of radiochemical version of neutron activation analysis for chromium determination in biological samples has allowed for the elimination of the interferences and has resulted in the lower limit of detection [29]. In this work we used Dowex 1X8 impregnated with saturated potassium permanganate solution for chromium separation and preconcentration. We examined resins with batch and column experiments. The results obtained for MnO_2 Resin and potassium permanganate impregnated Dowex 1X8 were compared. The results allowed to develop a procedure for the radiochemical determination of chromium in biological samples.

Experimental

Chromium standards for irradiation were prepared by weighing aliquots of the standard solution in polyethylene capsules (Type “V” Vrije Universiteit, Biologisch Laboratorium, Netherlands) and evaporating to dryness before encapsulation. The following radioactive tracers were used: ^{134}Cs ($T_{1/2}=2.06$ y), ^{60}Co ($T_{1/2}=5.27$ years), ^{51}Cr ($T_{1/2}=27.7$ days), ^{46}Sc ($T_{1/2}=83.8$ days), ^{65}Zn ($T_{1/2}=244$ days). All tracers were prepared by neutron irradiation of spectrally pure oxides or salts (mostly nitrates) in a Polish nuclear reactor MARIA (neutron flux of $10^{14} \text{ cm}^{-2} \text{ s}^{-1}$). All reagents were of analytical grade. MnO_2 Resin 100–200 mesh (Eichrom Technologies LLC) was used as received. High purity water, 18 M Ω cm from Milli QRG Ultra Pure Water System, Millipore Co., was used for the preparation of all solutions.

Preparation of manganese dioxide impregnated resin

A mass of 40 g of Dowex 1X8 [Cl^-] resin (100–200 mesh), was washed twice with water from the Millipore system (reverse osmosis). The anion exchanger was then flooded with 40 mL of previously prepared saturated KMnO_4 solution and stirred vigorously for 15 min. After that time the sample was centrifuged and the liquid from the sediment was poured off. The ionite impregnated with manganese groups was washed with 80 mL of distilled water of high purity, which was then centrifuged and washed away from the surface of the exchanger. This action was repeated three times. The resins prepared in this way were filtered and quantitatively transferred to a beaker. The exchanger was dried at 70 °C overnight and then gently mixed. The prepared resins were used in studies allowing for the determination of weight distribution coefficients.

Apparatus

Micro-analytical and analytical balances, Sartorius MC5 and Sartorius BP221S calibrated by the Central Office of Measures, were used to prepare standards, CRMs and samples for irradiation.

A high-pressure microwave system Anton Paar 3000 was applied to digest the samples.

Gamma-ray spectroscopic measurements were performed with the aid of a 255 cm^3 HPGe well-type (Canberra) detector with associated electronics (resolution 2.15 keV for 1332 keV ^{60}Co line, efficiency approximately 40% of a NaI (TI) detector), coupled to the multichannel analyser and Genie-2000 spectroscopy software (Canberra).

Glass columns of I.D. 0.50 cm were used in column experiments.

Determination of distribution coefficient

Mass distribution coefficients of ^{51}Cr and selected elements were determined in the system: MnO_2 Resin or manganese dioxide impregnated Dowex 1X8 resin—in hydrochloric, nitric and sulphuric acids by a batch equilibrium method at room temperature. Radioactive tracers of ^{134}Cs , ^{51}Cr , ^{65}Zn , ^{46}Sc , ^{60}Co were used. A 0.2 g amount of the MnO_2 Resin or manganese dioxide impregnated Dowex 1X8 resin was weighed into a plastic flask, and 10 mL of hydrochloric, nitric or sulphuric acids solution and radioactive tracers of the elements examined were added. After 24 h shaking at room temperature, the resin was separated by filtration and

the content of the radionuclide in the solution was measured by gamma spectrometry. The distribution coefficients were calculated from the equation:

$$K_d = \frac{A_0 - A_s}{A_s} \times \frac{V}{m_j} \quad (1)$$

where A_0 : the count rate of individual tracer in the standard solution; A_s : is the count rate of individual tracer in an aliquot of the solution, after equilibration with the resin, loaded with a given reagent, V : volume of the solution (mL); and m_j : mass of dry resin (g).

Column experiments

In column experiments we used a previously calibrated column ($h = 10$ cm, $r = 0.25$ cm) filled with MnO_2 Resin or Dowex 1X8 resin impregnated with potassium permanganate. For the column experiment, we used the radioactive tracers ^{134}Cs , ^{51}Cr , ^{65}Zn , ^{46}Sc , ^{60}Co . We prepared test and standard samples which contained the same radioactive tracers. Test samples were placed onto the column, and after the separation process measured with gamma spectrometry and compared with standard.

Results and discussion

MnO_2 Resin (Eichrom) and potassium permanganate impregnated Dowex 1X8 resin were tested for chromium sorption. In Figs. 1, 2 and 3 we show results from batch experiments for commercially available resin MnO_2 Resin (Eichrom) for chromium and other elements (Cs, Sc, Zn, Co). Figures 1, 2

Fig. 1 Mass distribution coefficients of ^{51}Cr (Cr(VI)) and ^{134}Cs , ^{46}Sc , ^{65}Zn and ^{60}Co on MnO_2 Resin in sulphuric acid (concentration range 0.01–2 mol/dm³)

Fig. 2 Mass distribution coefficients of ^{51}Cr (Cr(VI)) and ^{134}Cs , ^{46}Sc , ^{65}Zn and ^{60}Co on MnO_2 Resin in hydrochloric acid (concentration range 0.01–2 mol/dm³)

and 3 shows mass distribution coefficients in different concentrations of inorganic acids in range 0.01–2 mol/dm³.

As it can be seen in the Figs. 1, 2 and 3 sorption of chromium(VI) ions on MnO_2 Resin occurs preferably from dilute solutions of hydrochloric, nitric and sulphuric acids (0.01 mol/dm³). The highest mass distribution coefficient is observed in 0.01 mol/dm³ sulphuric acid. The sorption of chromium decreases when the concentration of acids increases. The mass distribution coefficient for other elements (Cs, Sc, Zn) in applied conditions were not high (excluding Co in 0.01 mol/dm³ HCl).

In Figs. 4, 5 and 6 we show the results from batch experiments for potassium permanganate impregnated Dowex 1X8 resin.

As it can be seen from Figs. 4, 5 and 6, sorption of chromium(VI) ions on impregnated Dowex 1X8 resin also occurs from diluted solutions of inorganic acids. The highest

Fig. 3 Mass distribution coefficients of ^{51}Cr (Cr(VI)) and ^{134}Cs , ^{46}Sc , ^{65}Zn and ^{60}Co on MnO_2 Resin in nitric acid (concentration range 0.01–2 mol/dm³)

Fig. 4 Mass distribution coefficients of ^{51}Cr (Cr(VI)) and ^{134}Cs , ^{46}Sc , ^{65}Zn and ^{60}Co on impregnated Dowex 1X8 resin in sulphuric acid (concentration range 0.01–2 mol/dm 3)

Fig. 5 Mass distribution coefficients of ^{51}Cr (Cr(VI)) and ^{134}Cs , ^{46}Sc , ^{65}Zn and ^{60}Co on impregnated Dowex 1X8 resin in hydrochloric acid (concentration range 0.01– mol/dm 3)

Fig. 6 Mass distribution coefficients of ^{51}Cr (Cr(VI)) and ^{134}Cs , ^{46}Sc , ^{65}Zn and ^{60}Co on impregnated Dowex 1X8 resin in nitric acid (concentration range 0.01–2 mol/dm 3)

Fig. 7 Separation of chromium from selected elements on MnO_2Resin in 0.01 mol/dm 3 H_2SO_4 (column experiment)

Fig. 8 Separation of chromium from selected elements on impregnated with potassium permanganate Dowex 1X8 resin in 0.01 mol/dm 3 HNO_3 (column experiment)

mass distribution coefficient for chromium was observed in 0.01 mol/dm 3 HNO_3 . The sorption of chromium ions (similarly for MnO_2Resin) decreases with increase of acids concentrations. The mass distribution coefficient for Cr(VI) on impregnated Dowex 1X8 resin is much smaller than for commercially available MnO_2Resin . Probably the reason for this was heterogeneous planting of impregnated resin with manganese groups. The mass distribution coefficients for other examined elements were very small (Cs, Sc), but we observed sorption of cobalt in 0.01 mol/dm 3 nitric acid. For Zn, the highest mass distribution coefficient was obtained in 2 mol/dm 3 hydrochloric acid.

The results from batch experiments were verified with a series of column experiments. For MnO_2Resin we have chosen 0.01 mol/dm 3 sulphuric acid, for impregnated Dowex 1X8 resin, 0.01 mol/dm 3 nitric acid, because the sorption of chromium in these media was the highest. The results obtained for MnO_2Resin are shown in Fig. 7, and for impregnated Dowex 1X8 resin in Fig. 8.

In Figs. 7 and 8 we show the separation process of chromium on MnO_2Resin and impregnated Dowex 1X8 resin.

Table 1 Determination of Cr in certified reference materials after separation with MnO₂Resin

CRM	Cr certified value and its confidence limit (95%)	Cr Obtained result $X \pm U$ ($k=2$)
IAEA-392 algae	$4.57 \pm 0.18 \text{ mg kg}^{-1}$	$4.58 \pm 0.18 \text{ mg kg}^{-1}$
IAEA-336 lichen	$1.06 \pm 0.34 \text{ mg kg}^{-1}$	$1.05 \pm 0.04 \text{ mg kg}^{-1}$
NIST SRM 1566a oyster tissue	$1.43 \pm 0.46 \text{ mg kg}^{-1}$	$1.41 \pm 0.04 \text{ mg kg}^{-1}$
MODAS M-3 herring tissue	$919 \pm 105 \text{ ng g}^{-1}$	$1030 \pm 30 \text{ ng g}^{-1}$

As can be seen chromium is completely separated from other elements in both cases studied. However in the case of manganese dioxide impregnated resin the shape of the chromium elution curve suggests the possibility of the presence of two forms of chromium. This also confirms the recovery of chromium after the separation process onto the column. The process is quantitative only in the case of MnO₂Resin and we have chosen this resin for further research on chromium determination in biological samples.

Chromium determination in biological samples after the separation with MnO₂Resin

In our work, we determined chromium in biological samples with radiochemical neutron activation analysis. Chromium is determined via ⁵¹Cr formed after reaction ⁵⁰Cr (n, γ) ⁵¹Cr, with half-life ($T_{1/2} = 27.7$ days) and 320 keV line in gamma spectrum. Radiochemical neutron activation analysis is an analytical method, where the test samples are irradiated in neutron flux (usually in nuclear reactor) and after that, the separation process of selected element is carried out. Separation process can be carried out with different methods, for example: extraction, distillation, precipitation or ion chromatography. As a result, for the separation process, we minimized the influence from other elements which occur in biological matrix (⁴⁰K, ²⁴Na, ³²P). For quantitative and selective separation of chromium from biological matrix we used previously checked by batch and column experiments MnO₂Resin. The separation process was carried out in the same way like the column experiments on MnO₂Resin. The irradiated samples were digested using a microwave system and the resulting solution was evaporated and dissolved in 0.01 mol/dm³ H₂SO₄. The obtained solution was introduced onto the top of a column filled with resin and the elution process started. Impurities were eluted by washing with first 0.1 mol/dm³ HNO₃, and then with 4 mol/dm³ HCl. Chromium was quantitatively eluting with 8 mol/dm³ H₂SO₄. The procedure was checked by analysis of several certified references materials. The results are presented in Table 1.

As it can be seen from Table 1, the results obtained for chromium after separation process using MnO₂Resin, agree very well with certified values. The analysis of several

certified references materials confirms the high accuracy of the developed procedure. The detection limit calculated with the Curie equation is 4.9 ng g⁻¹ (20,000 s counting time) [30].

Conclusion

MnO₂Resin and Dowex 1X8 impregnated with potassium permanganate resin was used for chromium preconcentration and separation from other elements. Chromium has a high affinity to both resins. However, the K_d values for chromium were higher in MnO₂Resin than for Dowex 1X8 impregnated resin. The column experiments show that the separation process of chromium from other elements is selective but only in the case of MnO₂Resin was quantitative and selective. The procedure of quantitative separation of chromium on MnO₂Resin was checked by analysis of several certified references materials. The results show agreement with certified values, which confirms the accuracy of the developed procedure.

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