

$^{99}\text{Mo}/^{99\text{m}}\text{Tc}-^{113}\text{Sn}/^{113\text{m}}\text{In}$ Dual Radioisotope Generator Based on 6-Tungstocerate(IV) Column Matrix

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Elutions of $^{99\text{m}}\text{Tc}$ and $^{113\text{m}}\text{In}$ have been performed subsequently with 10 mL of 0.9% NaCl solution and 10 mL of 0.1 M HCl solution, respectively, from 6-tungstocerate(IV) chromatographic column loaded with 0.54 MBq ^{99}Mo and 0.45 MBq ^{113}Sn , using alumina-column filter in the case of $^{99\text{m}}\text{Tc}$. Radionuclidic purity of both eluates was $\geq 99.99\%$. Elution yields of $72.5\pm 5.8\%$ and $62.2\pm 3.7\%$, and radiochemical purities of $96.9\pm 1.0\%$ (as $^{99\text{m}}\text{TcO}_4^-$) and $88.4\pm 2.5\%$ (as $^{113\text{m}}\text{In}^{3+}$) have been obtained for $^{99\text{m}}\text{Tc}$ and $^{113\text{m}}\text{In}$, respectively. Al and W impurities in the $^{99\text{m}}\text{Tc}$ and $^{113\text{m}}\text{In}$ eluates, respectively, were found to be within the accepted limits, whereas no Ce impurities were detected in both eluates. Also trials have been carried out on a similar system to obtain mixed $^{99\text{m}}\text{Tc}-^{113\text{m}}\text{In}$ eluates from 6-tungstocerate column with different $^{99\text{m}}\text{Tc}/^{113\text{m}}\text{In}$ ratios using 0.9% NaCl-HCl eluents of different pH values. To separate $^{99\text{m}}\text{Tc}$ and $^{113\text{m}}\text{In}$ from each other, these mixed eluates were passed through a column of hydrous zirconium oxide which was then eluted with 10 mL of 0.9% NaCl solution and 15 mL of 0.1 M HCl solution, respectively. No W, Ce, or Zr impurities were detected in the $^{99\text{m}}\text{Tc}$ and $^{113\text{m}}\text{In}$ eluates obtained in these trials.

1. Introduction

$^{99\text{m}}\text{Tc}$ ($t_{1/2} = 6.01$ h) and $^{113\text{m}}\text{In}$ ($t_{1/2} = 1.66$ h) are suitable radionuclides for diagnostic purposes in nuclear medicine because of (i) short physical half-lives, (ii) very low-abundance of β^- -emission for $^{99\text{m}}\text{Tc}$ and its absence in the case of $^{113\text{m}}\text{In}$, (iii) γ -emissions of suitable energy for imaging processes [140.5 keV (89.4%) and 391.7 keV (64.2%) for $^{99\text{m}}\text{Tc}$ and $^{113\text{m}}\text{In}$, respectively].¹ $^{99\text{m}}\text{Tc}$ (VII)-pertechnetate is used for brain, thyroid, salivary gland, and lachrymal duct scintigraphy and imaging of gastric mucosa.² Also different $^{99\text{m}}\text{Tc}$ -radiopharmaceutical compounds are used for detection of lung cancer, cardiac blood pool imaging, liver and spleen scintigraphy, etc.^{2,3} Carrier-free $^{113\text{m}}\text{In}$ in 2% gelatin (pH 4) is used for "vascular-pool" imaging applications.⁴ $^{113\text{m}}\text{In}$ -labeled compounds can be used for lung and liver scanning,⁵ and for brain imaging applications.⁶ $^{113\text{m}}\text{In}$ can also be used as a radiotracer to study the flow behavior of crude oil in a battery of industrial crude oil/gas separators in oil industry.⁷

Generally, dual isotope imaging, simultaneous imaging of two radionuclides, has been successively used in various clinical applications. This technique is advantageous over single isotope imaging for the cases in which two assessments needed, where in the former technique these assessments can be carried out in a single examination. For instance, quantitative dual-isotope SPET technique has been utilized for the assessment of lung ventilation and perfusion simultaneously using $^{99\text{m}}\text{Tc}$ -labeled Technegas and $^{113\text{m}}\text{In}$ -labeled macro-aggregated albumin.⁸

$^{99\text{m}}\text{Tc}$ and $^{113\text{m}}\text{In}$ are nuclear-decay products of ^{99}Mo ($t_{1/2} = 65.94$ h) and ^{113}Sn ($t_{1/2} = 115.09$ d) radionuclides, respectively,¹ and they are usually obtained by periodical elution from $^{99}\text{Mo}/^{99\text{m}}\text{Tc}$ and $^{113}\text{Sn}/^{113\text{m}}\text{In}$ radioisotope generators, respectively, based on chromatographic columns. However, examples for less famous solvent extraction⁹⁻¹¹ and sublimation $^{99}\text{Mo}/^{99\text{m}}\text{Tc}$ generators¹²⁻¹⁴ have been reported in literature. (n,f) ^{99}Mo is loaded onto alumina chromatographic columns,¹⁵⁻¹⁷

whereas (n, γ) ^{99}Mo can be loaded onto or incorporated into different gel materials (e.g. tin molybdate, zirconium molybdate, 12-molybdocerate(IV), and titanium molybdate) which packed in chromatographic columns.¹⁸⁻²² $^{99\text{m}}\text{Tc}$ is usually eluted from these columns using 0.9% NaCl. Subramanian and McAfee,²³ and Lin et al²⁴ studied separately the use of hydrous zirconium oxide (HZO) column for adsorption of ^{113}Sn from 0.3–0.5 M and 0.2 M HCl, respectively, and elution of $^{113\text{m}}\text{In}$ with 0.1 M HNO_3 (or 0.1 M HCl) and 0.05 M HCl, respectively. Arino and Kramer²⁵ studied the chemical sorption of ^{113}Sn (IV) separately on HZO and silica gel by heating in the presence of bromine water and 0.4 M HCl. $^{113\text{m}}\text{In}$ (III) was eluted in both cases with a high separation Sn/In factor ($> 10^4$) using HCl solution of $\text{pH} > 1.2$. El-Said²⁶ used 12-molybdocerate(IV) column for sorption of ^{113}Sn (IV) from 0.1 M HCl solution and elution of $^{113\text{m}}\text{In}$ (III) using the same solution. Teranishi et al²⁷ reported the adsorption of ^{113}Sn (IV) on a column of glass beads from 0.16 M NaCl solution and elution of $^{113\text{m}}\text{In}$ (III) with the same solution.

Mostafa²⁸ successfully prepared $^{99}\text{Mo}/^{99\text{m}}\text{Tc}-^{137}\text{Cs}/^{137\text{m}}\text{Ba}$ dual radioisotope generator based on 6-tungstocerate(IV)(6-WCe) from which $^{99\text{m}}\text{Tc}$ and $^{137\text{m}}\text{Ba}$ were subsequently eluted ($^{137\text{m}}\text{Ba}$ was eluted after decay of ^{99}Mo) using 0.9% NaCl and 0.9% NaCl-HCl (pH 1) solutions, respectively.

This work aims at preparation of $^{99}\text{Mo}/^{99\text{m}}\text{Tc}-^{113}\text{Sn}/^{113\text{m}}\text{In}$ dual radioisotope generator based on 6-WCe chromatographic column from which $^{99\text{m}}\text{Tc}$ and $^{113\text{m}}\text{In}$ can be eluted simultaneously or subsequently (i.e. eluting $^{113\text{m}}\text{In}$ after decay of ^{99}Mo) with high-purity suitable for use in different medical applications.

2. Experimental

2.1. Chemicals and instruments. All chemicals used in the present work were of AR grade. Distilled water was used for solution preparation. Gamma-ray spectrometer consisting of a multichannel analyzer (MCA) of "Inspector 2000" model, Canberra Series, made in USA, coupled with a high-purity germanium coaxial detector (HPGe) of GX2518 model was used for γ -radioactivity measurements. The assignment of γ -photo-

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peaks obtained in the γ -ray spectra to the corresponding radionuclides was cited from Chu et al.¹ A NaI (TI) γ -ray scintillation counter of "Scaler Ratemeter SR7" model, made in England, was used for measurements of gross γ -radioactivities of eluate solutions. Jenway 6405 UV-VIS spectrophotometer, made in U.K., was used for detection of Ce and W impurities in eluate solutions. Sequential plasma emission spectrometer of "ICPS-7500" type, Shimadzu, made in Japan, was used for detection of Al impurities in eluate solutions. pH-meter with microprocessor of "pH211" model, Hanna Instruments, made in Portugal, was used for measurement of pH values of different solutions.

2.2. Preparation of ^{99}Mo and ^{113}Sn solutions. Carrier-free ^{99}Mo was obtained by elution of Mon-Tek $^{99}\text{Mo}/^{99\text{m}}\text{Tc}$ generator (Monrol Nuclear Products Industry and Trade Inc. made in Turkey) after 25 d from its calibration date (loaded with 20 GBq of ^{99}Mo on its calibration date) with 1 M of NaOH solution. The ^{99}Mo eluate solution was passed through 0.45- μm millipore filter to retain any possible contained alumina particles. Then, ^{99}Mo solution was diluted with HCl solution to the desired pH-value. To obtain ^{113}Sn solution, tin powder targets (irradiated in the Second Egyptian Nuclear Reactor, ETRR-II, for 4 h at a thermal-neutron flux of $1 \times 10^{14} \text{ n cm}^{-2} \text{ s}^{-1}$ and cooled for 28 d), 0.1 g of each, was dissolved in concentrated HCl solution warmed at $\sim 50^\circ\text{C}$ in a water bath with a stepwise addition of few H_2O_2 drops, to accelerate the dissolution rate. After dissolution of the tin target, further few drops of H_2O_2 were added to ensure the complete oxidation of Sn(II) to Sn(IV). The complete oxidation was checked using ammonium molybdate solution, where the blue color indicates the presence of Sn(II).²⁹ Thereafter, the solution was evaporated to few drops at $\sim 60^\circ\text{C}$, left to cool to room temperature, and finally diluted to the desired concentration using HCl solution.

2.3. Preparation of 6-tungstocerate(IV), 6-WCe, gel matrix. The preparation method of 6-WCe gel stated by El-Amir³⁰ was followed. 500 mL of 0.3 M tungstate(VI) solution, prepared by dissolution of 49.5 g of $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ in dilute H_2SO_4 (pH 1), was maintained at 100°C for ~ 15 min and left to cool at room temperature. Thereafter, 500 mL of 0.05 M ammonium cerium(IV) sulfate solution, prepared by dissolution of 15.8 g of $\text{Ce}(\text{SO}_4)_2 \cdot 2(\text{NH}_4)_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$ in dilute H_2SO_4 acid (pH 1), was added to the tungstate(VI) solution under steady stirring at 25°C . The precipitate formed was separated by centrifugation and, then, thoroughly washed with distilled water, 2 M HCl, and again with distilled water till it became free from interstitial acid. The product material was dried at 50°C for 48 h and then pulverized to 0.12–0.24 mm particle size.

2.4. Preparation of hydrous zirconium oxide. Hydrous zirconium oxide (HZO) was prepared by the homogeneous precipitation method,³¹ in which 50 g/L $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ solution in 0.5 M HCl was added and mixed with urea (in the ratio of 100 mL solution : 15 g of urea). The resulting solution was heated to 90°C on a hot plate. After formation of HZO precipitate, the mixture was kept at 90°C for additional 1 h. The precipitate was filtered and washed repeatedly with distilled water for the removal of chloride traces and, then, dried at room temperature in a desiccator.

2.5. Batch distribution studies. The distribution coefficients of (i) ^{99}Mo and $^{99\text{m}}\text{Tc}$ and (ii) ^{113}Sn and $^{113\text{m}}\text{In}$ couples between 10 mL (V) of aqueous phases of carrier-free ^{99}Mo (in equilibrium with $^{99\text{m}}\text{Tc}$) and of 1×10^{-4} M Sn(IV) (in equilibrium with $^{113\text{m}}\text{In}$) in 0.1 M NaCl–HCl and HCl solutions, respectively, of different pH values and 0.1-g amounts of 6-WCe gel matrix (m) were determined by equilibrating their mixtures separately in 20-mL glass vials which in turn were placed in a water-bath thermostat shaker for 24 hours at $25 \pm 1^\circ\text{C}$. The distribution coefficient, K_d (mL/g), at different pH values was calculated from the following equation:

$$K_d = \frac{A_0 - A_e}{A_e} \times \frac{V}{m} \quad (\text{mL/g}), \quad (1)$$

where A_0 and A_e are the counting rates (cpm) of the radionuclide of interest in the aqueous phase before and after contact with the gel matrix, respectively.

2.6. Loading capacity studies of 6-WCe gel matrix for Sn(IV). Loading capacity was determined by batch equilibration method, in which 0.1 g of 6-WCe gel matrix was repeatedly equilibrated with 10 mL of a freshly prepared 0.1 M HCl solution containing 10^{-2} M Sn(IV) in a 20-mL glass vial placed in a water-bath thermostat shaker at $25 \pm 1^\circ\text{C}$ until saturation was attained, as indicated by obtaining a constant counting rate of the aqueous phase before and after equilibration with the gel matrix.

2.7. Radioisotope dual generator system. A glass column of 0.7 cm i.d., with a small piece of glass wall plug at its bottom followed by a stopcock, was packed with 1 g of 6-WCe gel matrix by settling from distilled water. The column was conditioned with 20 mL of 0.1 M NaCl–HCl solution (pH 1) and subsequently loaded with 35 mL of an identical solution containing carrier-free ^{99}Mo (VI) (0.54 MBq). Thereafter, the column was further conditioned with 20 mL of 0.1 M HCl and subsequently loaded with 168 mL of an identical solution of 5×10^{-3} M Sn(IV) (0.45 MBq ^{113}Sn). The flow rate of loading of both solutions was 1 mL/min. The column was conditioned with 20 mL of 0.9% NaCl solution. After 23 h, $^{99\text{m}}\text{Tc}$ was eluted with 10 mL of 0.9% NaCl solution. $^{99\text{m}}\text{Tc}$ eluate was passed through an alumina column (0.7 cm i.d.) packed with 1 g alumina preconditioned with 20 mL of 0.9% NaCl solution. The alumina column was then eluted with 10 mL of 0.9% NaCl solution. 14 elution processes of $^{99\text{m}}\text{Tc}$ have been performed along 21 d. After practical complete decay of ^{99}Mo (60 d), 6-WCe column was conditioned with 20 mL of 0.1 M HCl solution. After 18 h, $^{113\text{m}}\text{In}$ was eluted with 10 mL of 0.1 M HCl solution. 100 elution processes of $^{113\text{m}}\text{In}$ have been performed along 6 months. On the other hand, trials have been performed on a parallel similar system to obtain mixed $^{99\text{m}}\text{Tc}$ – $^{113\text{m}}\text{In}$ eluates using 0.9% NaCl–HCl eluents of different pH values. These eluates were passed through a column (0.7 cm i.d.) of 0.6 g HZO preconditioned with 20 mL of 0.9% NaCl solution, which was then eluted with 10 mL of 0.9% NaCl and 15 mL of 0.1 M HCl, respectively.

2.8. Quality control of $^{99\text{m}}\text{Tc}$ and $^{113\text{m}}\text{In}$ eluates. Elution yields of $^{99\text{m}}\text{Tc}$ and $^{113\text{m}}\text{In}$ were determined by comparing the counting rates of these radionuclides on the column before and after elution using the γ -ray spectrometer. Radionuclidic purity was determined by using the γ -ray spectrometer to determine the contribution of any possible radiocontaminants, if present, and was verified by tracing their nuclear decay with time, using the γ -ray scintillation counter, to determine the corresponding half-life. pH values of the eluate solutions were determined using the pH-meter. Radiochemical purity of the eluates, the contribution of the desired chemical form of $^{99\text{m}}\text{Tc}$ and $^{113\text{m}}\text{In}$ in their eluates, were determined by the ascending paper chromatography technique using Whatman No.1 chromatographic paper and a mixture of 85% methanol + 15% H_2O in the case of $^{99\text{m}}\text{Tc}$, and 90% ethanol + 10% of 5 M HCl in the case of $^{113\text{m}}\text{In}$, as developing solvents. The radioactivity distributions along the obtained chromatograms were traced, using the γ -ray scintillation counter, to determine R_f -values, where:

$$R_f = \frac{\text{traveled distance of the radioactivity from the start point to the peak position}}{\text{traveled distance of the solvent from the start point to the solvent front}}. \quad (2)$$

Tungsten and cerium impurities, originated from 6-WCe gel matrix, were determined in $^{99\text{m}}\text{Tc}$ and $^{113\text{m}}\text{In}$ eluates spectrophoto-

tometrically at wavelengths of 403 nm (by using the thiocyanate method) and 320 nm (by using the persulfate method), respectively,^{32,33} using the UV-VIS spectrophotometer. Aluminum impurities, originated from the alumina-filter column, in $^{99\text{m}}\text{Tc}$ elutes were determined by using the plasma emission spectrometer at wavelength of 308.22 nm.³⁴ Zirconium impurities, originated from HZO column, in $^{99\text{m}}\text{Tc}$ and $^{113\text{m}}\text{In}$ eluates were determined spectrophotometrically at wavelength of 665 nm (by using the arsenazo-III method).³⁵

3. Results and discussion

^{99}Mo was obtained as MoO_4^{2-} from the $^{99}\text{Mo}/^{99\text{m}}\text{Tc}$ generator using 1 M NaOH as an eluent,³⁶ whereas ^{113}Sn solution was obtained by dissolution of the irradiated tin in concentrated HCl and oxidation with H_2O_2 to obtain SnCl_6^{2-} .³⁷ 6-WCe gel matrix was chosen as a base matrix due to its chemical, radiation, and thermal stability in addition to its reliable use as a base matrix of $^{188}\text{W}/^{188\text{m}}\text{Re}$, $^{137}\text{Cs}/^{137\text{m}}\text{Ba}$, and dual $^{137}\text{Cs}/^{137\text{m}}\text{Ba}-^{99}\text{Mo}/^{99\text{m}}\text{Tc}$ radioisotope generators.^{28,30,38}

3.1. Batch distribution studies of ^{99}Mo and $^{99\text{m}}\text{Tc}$. Figure 1 shows distribution coefficients of ^{99}Mo and $^{99\text{m}}\text{Tc}$ in 0.1 M NaCl–HCl media as functions of pH of the equilibrating solution. As shown in Figure 1, K_d of molybdenum increases with decreasing pH value, where it increases gradually from 153 ± 10 to 279 ± 12 mL/g with decreasing pH from 12.4 to 2.4 and then increases abruptly to reach 492 ± 7 mL/g at pH 1. K_d of technetium increases with decreasing pH nearly parallel to that of molybdenum but with much less values; it increases gradually from 25 ± 2 to 37 ± 2 mL/g with decreasing pH from 12.4 to 2.4 and then increases abruptly to 67 ± 2 mL/g at pH 1. Along the studied pH range (1–12.4), molybdenum exists in solution as anionic species; $[\text{MoO}_4]^{2-}$ predominates at $\text{pH} > 6$, $[\text{Mo}_7\text{O}_{24}]^{6-}$ predominates at $\text{pH} 1.5\text{--}3.5$, while $[\text{Mo}_8\text{O}_{26}]^{4-}$ predominates at $\text{pH} 1$.^{20,36,38} 6-WCe was prepared and characterized before as a cation exchanger^{28,30} and therefore the uptake of ^{99}Mo cannot be interpreted by ion-exchange mechanism. Since 12-tungstocerate(IV), 12-WCe, and 12-molybdocerate, 12-MoCe, could be prepared and characterized,^{30,38} there are 6 vacant octahedral sites around the tetrahedron of the central cerium heteroatom in 6-WCe, the uptake of ^{99}Mo may be interpreted by the formation of a 6-WCe–6-MoCe mixed heteropolyacid of a suggested chemical composition of $[\text{CeO}_4 \cdot \text{W}_6\text{Mo}_6\text{O}_{36}]^{4-} \cdot x\text{H}_2\text{O}$.^{30,40–43} The increase of K_d of technetium with decreasing pH in such manner is attributed to the predominance of TcO_4^- anionic species in slightly acidic and moderate alkali pH values and the formation of the reduced technetium species, e.g. $[\text{TcCl}_4(\text{H}_2\text{O})_2]$ and $[\text{TcCl}_3(\text{H}_2\text{O})_3]^+$, in more acidic pH values.^{44,46} The higher K_d -values of molybdenum compared to those of technetium at the corresponding pH values supports the possibility of the formation of 6-WCe–6-MoCe mixed heteropolyacid.

3.2. Batch distribution studies of ^{113}Sn and $^{113\text{m}}\text{In}$. Figure 2 shows distribution coefficients of ^{113}Sn and $^{113\text{m}}\text{In}$ in HCl media as functions of pH of the equilibrating solution. It is obvious that K_d of tin increases from 142 ± 25 to 1868 ± 37 mL/g with increasing pH from 0.7 to 1.1 and shows only a minor increase in the pH range from 1.1 to 2.3 (2205 ± 57 mL/g at $\text{pH} 2.3$). K_d of indium shows similar behavior, but with much less values; it sharply increases from 3 ± 1 to 22 ± 4 mL/g with increasing pH from 0.7 to 1.1 and shows a little increase in the pH range from 1.1 to 2.3 (31 ± 4 mL/g at $\text{pH} 2.3$). The high K_d -values of tin and indium in the pH range of 1.1–2.3 may be due to the predominance of cationic species of tin $[\text{Sn}(\text{OH})^{3+}$, $\text{Sn}(\text{OH})_2^{2+}$, and $\text{Sn}(\text{OH})_3^+$] and $\text{Sn}(\text{OH})_4$ as well as cationic species of indium $[\text{In}^{3+}$, InCl^{2+} , InCl_2^+ , $\text{In}(\text{OH})^{2+}$, and $\text{In}(\text{OH})_2^+$] which retained onto the 6-WCe matrix by ion exchange and/or hydrolytic mechanism.^{48–51} As stated for Mo/Tc couple, the

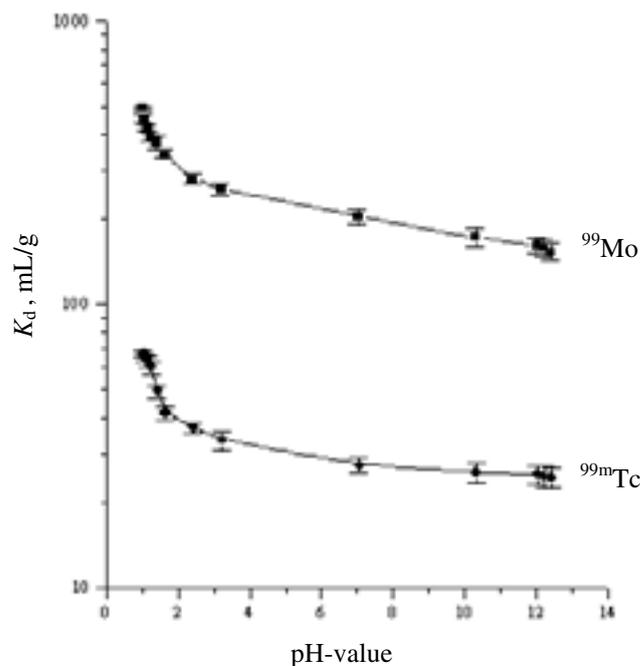


Figure 1. Distribution coefficients of ^{99}Mo and $^{99\text{m}}\text{Tc}$ in 0.1 M NaCl–HCl media as functions of pH of the equilibrating solution at 25 ± 1 °C.

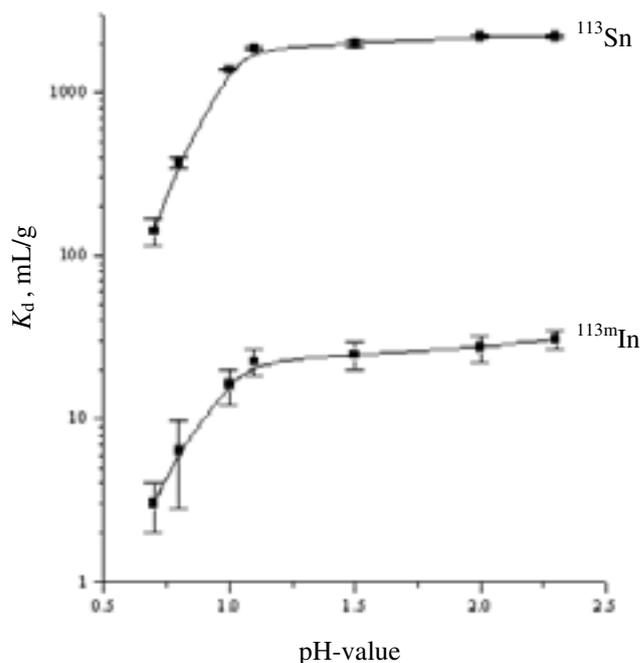


Figure 2. Distribution coefficients of ^{113}Sn and $^{113\text{m}}\text{In}$ in HCl media as functions of pH of the equilibrating solution at 25 ± 1 °C.

higher K_d -values of tin relative to those of indium may be attributed to the formation of tin tungstate⁵². Reactions between ^{99}Mo and ^{113}Sn with 6-WCe gel matrix to form 6-WCe–6-MoCe and tin tungstate compounds, respectively, were fast due to the pseudo-liquid behavior of 6-WCe, as a heteropolyacid, where the reaction field is three-dimensional (like that in liquid phase) because of the flexible lattice of 6-WCe.⁵³

3.3. Loading of ^{99}Mo solution. As indicated by batch distribution studies of ^{99}Mo , the highest K_d -value was obtained at pH 1 and hence the 6-WCe column was conditioned with 20 mL of 0.1 M NaCl–HCl solution (pH 1) and, subsequently, ^{99}Mo was loaded from an identical solution onto the column. Figure 3 shows the γ -ray spectra of (a) ^{99}Mo loading solution, (b) 6-WCe column after loading, and (c) loading effluent. Only

the γ -photopeaks of ^{99}Mo and $^{99\text{m}}\text{Tc}$ appear in the spectra of loading solution (a) and the column after loading (b). ^{99}Mo was quantitatively retained onto the 6-WCe column as indicated by the solely appearance of γ -photopeak of $^{99\text{m}}\text{Tc}$ (140 keV) in the loading effluent (c). Chemical composition of the loading solution could greatly change the % uptake of ^{99}Mo , since in a previous work³⁰, only ~ 69% of carrier-free ^{99}Mo (loaded from aqueous solution contained 5.7 M Na^+ , 2 M SO_4^{2-} , and 1.7 M NO_3^-) was retained onto 1.5-g 6-WCe column.

3.4. Loading of ^{113}Sn solution. Although the K_d -value of tin at pH 1 was not the highest one (Figure 2), tin was loaded onto the 6-WCe column (preconditioned with 20 mL of 0.1 M HCl) from 0.1 M HCl (pH 1) solution, since loading from solutions of higher pH values was not preferred to avoid the possibility of the bulk precipitation of $\text{Sn}(\text{OH})_3$, which in turn may cause blocking of the column. As indicated from the batch-loading capacity study, uptake value of 1 ± 0.2 mmol $\text{Sn}(\text{IV})/\text{g}$ 6-WCe was obtained. The amount of tin loaded onto the column containing 1 g of 6-WCe did not exceed this uptake value, since 168 mL of 5×10^{-3} M $\text{Sn}(\text{IV})$ solution in 0.1 M HCl, i.e. a solution contained 0.84 mmol $\text{Sn}(\text{IV})$, was passed through the

column. Figure 4 shows the γ -ray spectra of (a) ^{113}Sn loading solution, (b) 6-WCe column (previously loaded with ^{99}Mo) after loading with ^{113}Sn , and (c) loading effluent. γ -photopeaks of $^{113,117\text{m},119\text{m}}\text{Sn}$ and $^{124,125}\text{Sb}$ appear in the spectrum of the loading solution. As a result of concentration onto the 6-WCe column, ^{125}Sn and ^{134}Cs were detected, as indicated by their corresponding photopeaks in Figure 4 (b). According to Figure 4 (c), loading effluent contained $^{99\text{m}}\text{Tc}$ and $^{113\text{m}}\text{In}$ in addition to traces of ^{99}Mo , which may be unreacted and interstitially displaced by passing the loading solution of tin. Neither antimony nor cesium radioactive cross-contaminants was detected in the loading effluent. $^{134}\text{Cs}^+$ was strongly retained onto 6-WCe by ion exchange mechanism, where heteropolyacids have a high selectivity for monovalent large cations.^{38,54,55} According to John and Kahn,⁵⁴ $\text{Sb}(\text{III})/\text{Sb}(\text{V})$ ratio depends on the chlorine concentration according to the following reversible reaction:



Thus, the quantitative uptake of $^{124,125}\text{Sb}$ by the 6-WCe at pH 1 may suggest the retention of $\text{Sb}(\text{III})$, as $\text{Sb}(\text{OH})_2^+$ by ion-

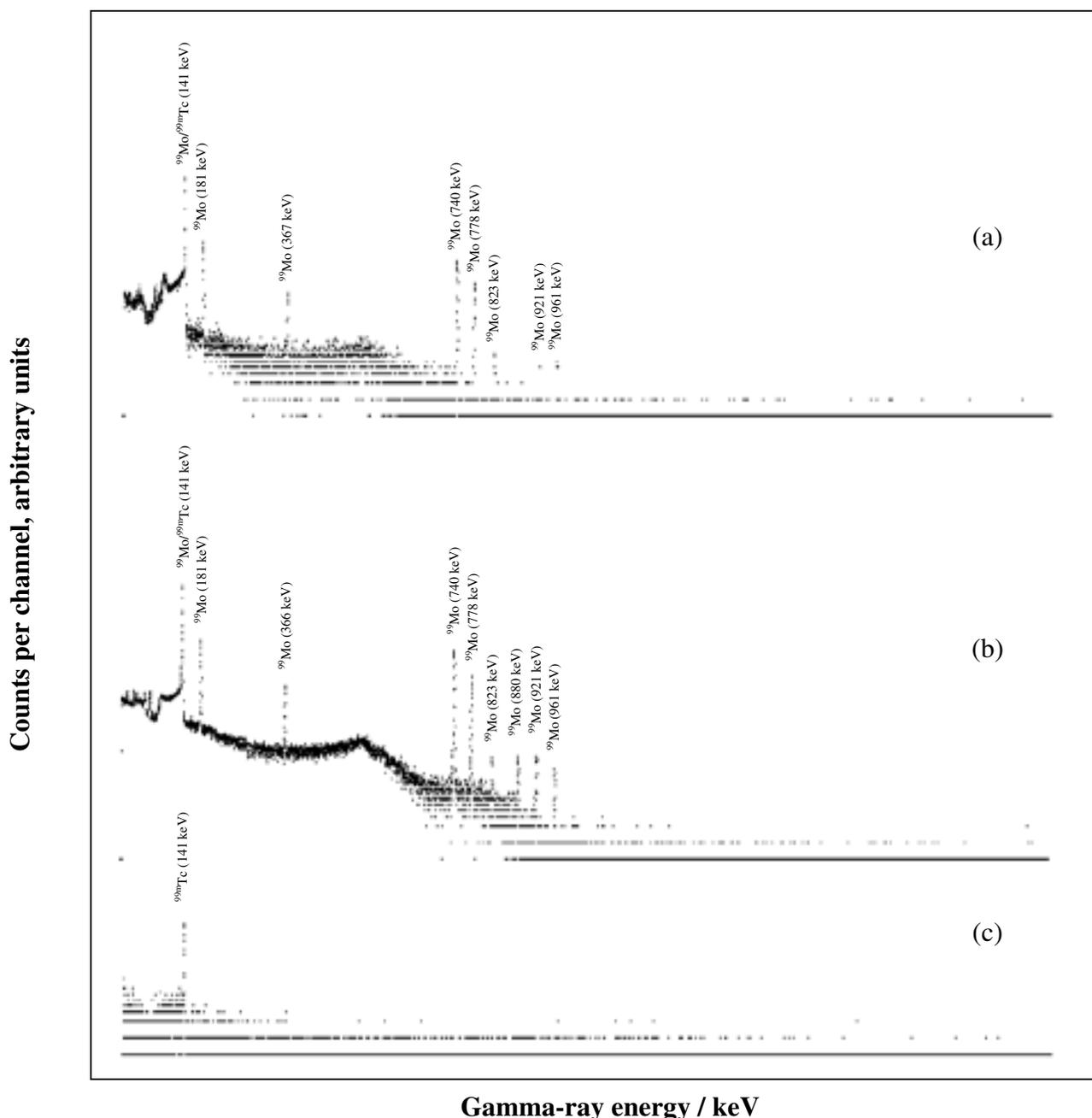
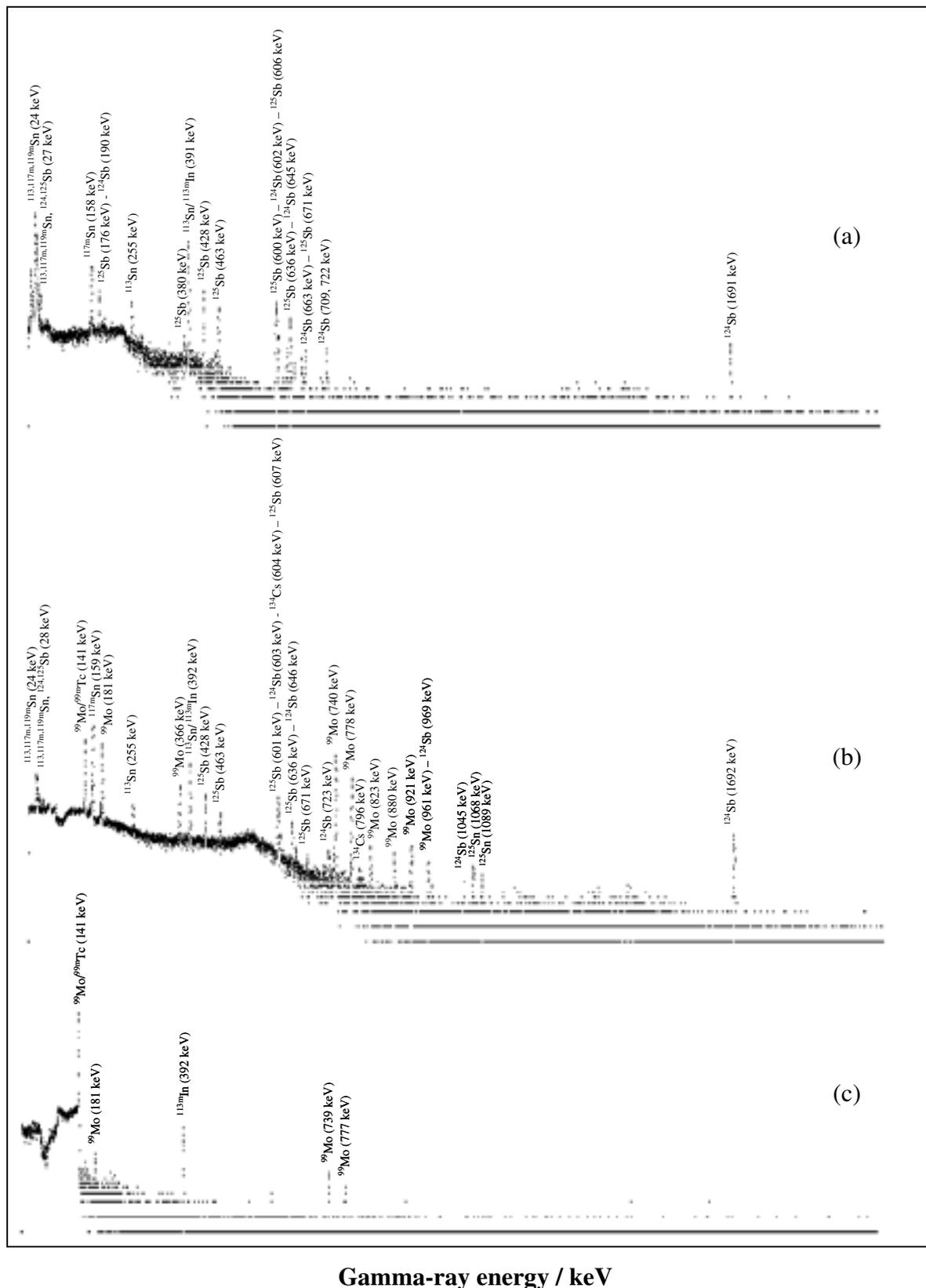


Figure 3. Gamma-ray spectra of (a) ^{99}Mo loading solution, (b) 6-WCe column after loading, and (c) loading effluent.

Counts per channel, arbitrary units



Gamma-ray energy / keV

Figure 4. Gamma-ray spectra of (a) ^{113}Sn loading solution, (b) 6-WCe column (previously loaded with ^{99}Mo) after loading with ^{113}Sn , and (c) loading effluent.

exchange (and/or hydrolytic mechanism) and/or retention of Sb(V) as $\text{HSb}(\text{OH})_6$ by coprecipitation, regarding the 6-WCe matrix as a carrier.⁵⁷

3.5. Elution of $^{99\text{m}}\text{Tc}$. After loading ^{99}Mo and ^{113}Sn subsequently onto 6-WCe column, the column was conditioned for $^{99\text{m}}\text{Tc}$ elution with 20 mL of 0.9% NaCl solution and, then, the column was eluted after 23 h with 10 mL of 0.9% NaCl solution. Figure 5 shows γ -ray spectra of 6-WCe loaded with ^{99}Mo and ^{113}Sn (a) before and (b) after elution with 0.9% NaCl solu-

tion, and (c) eluate. It was found that, the eluate contained both of $^{99\text{m}}\text{Tc}$ and $^{113\text{m}}\text{In}$ (Figure 5c). Along 21-d period from loading of ^{99}Mo and $^{113\text{m}}\text{Sn}$, radiometric calculations indicated that $72.5 \pm 5.1\%$ and $0.5 \pm 0.3\%$ of $^{99\text{m}}\text{Tc}$ and $^{113\text{m}}\text{In}$, respectively, were co-eluted with 10 mL of 0.9% NaCl solution. For example, 99.8% of the radioactivity of the first eluate was due to $^{99\text{m}}\text{Tc}$ while only 0.2% of it was due to $^{113\text{m}}\text{In}$. However, these contributions changed gradually ($\%^{99\text{m}}\text{Tc}$ decreased and $\%^{113\text{m}}\text{In}$ increased) as more ^{99}Mo decayed. After passing this eluate

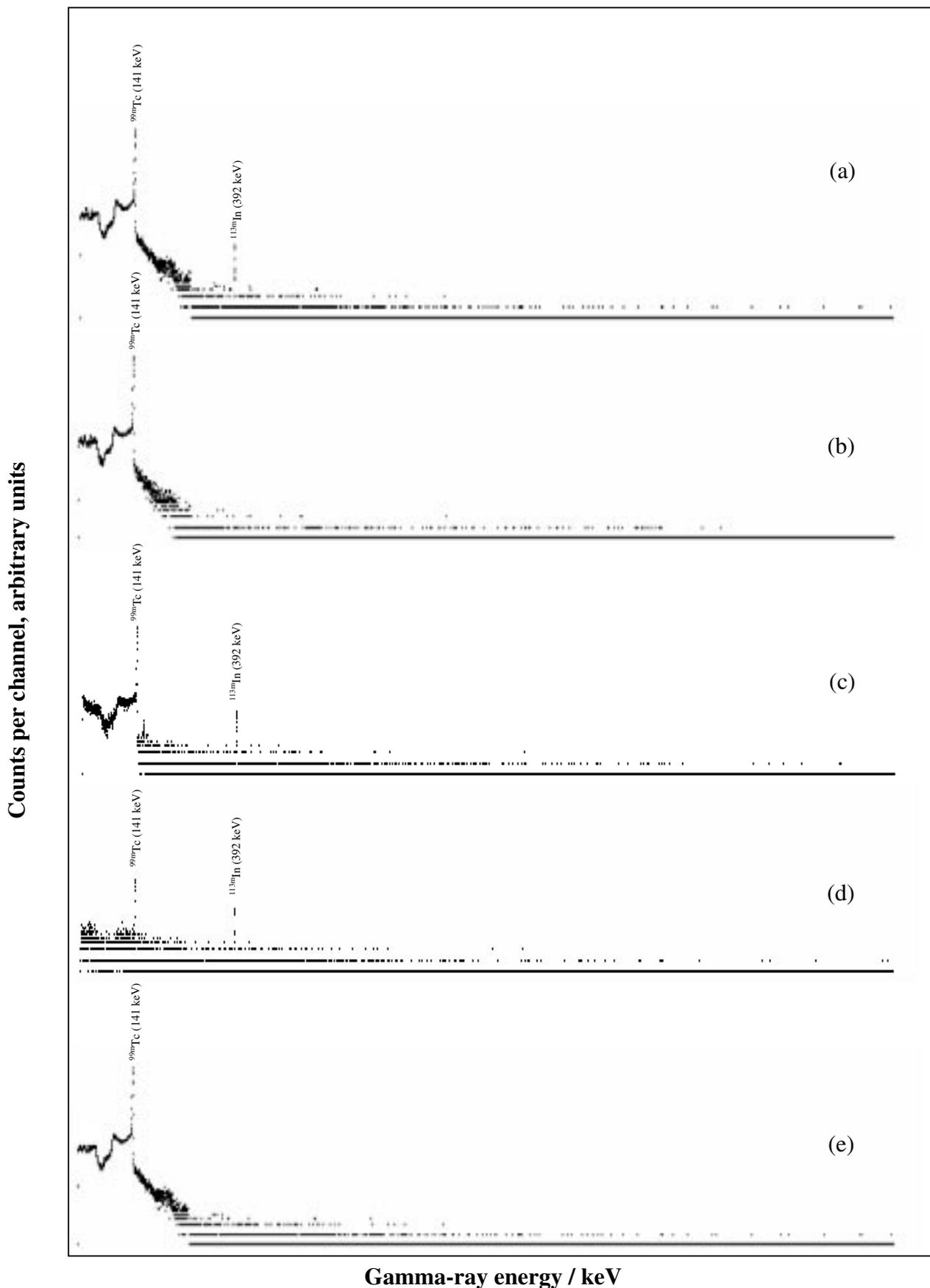


Figure 6. Gamma-ray spectra of $^{99\text{m}}\text{Tc}$ eluted from 6-WCe column (a) before and (b) after passing through alumina-column filter, and alumina-column filter (c) before and (d) after elution with 10 mL of 0.9% NaCl solution, and (e) eluate from the alumina-column filter.

$^{99\text{m}}\text{Tc}$ eluted from the 6-WCe column was concentrated in the first 3 mL, with a maximum value of 47.4% at 1 mL, while 15.5% was distributed in the last 7 mL of the eluate as a long tail. Figure 7 (b) shows a broad peak with three maxima for elution of $^{113\text{m}}\text{In}$ from the 6-WCe column; a higher maximum

value of 19.1% at 1 mL and two smaller maxima of 11.8 and 7.2% at 4 and 9 mL, respectively. According to Figure 7 (c), a sharp peak was obtained for elution of $^{99\text{m}}\text{Tc}$ from the alumina-column filter; 99.2% of $^{99\text{m}}\text{Tc}$ radioactivity was concentrated in the first 3 mL, with a maximum value of 64.9% at 2 mL,

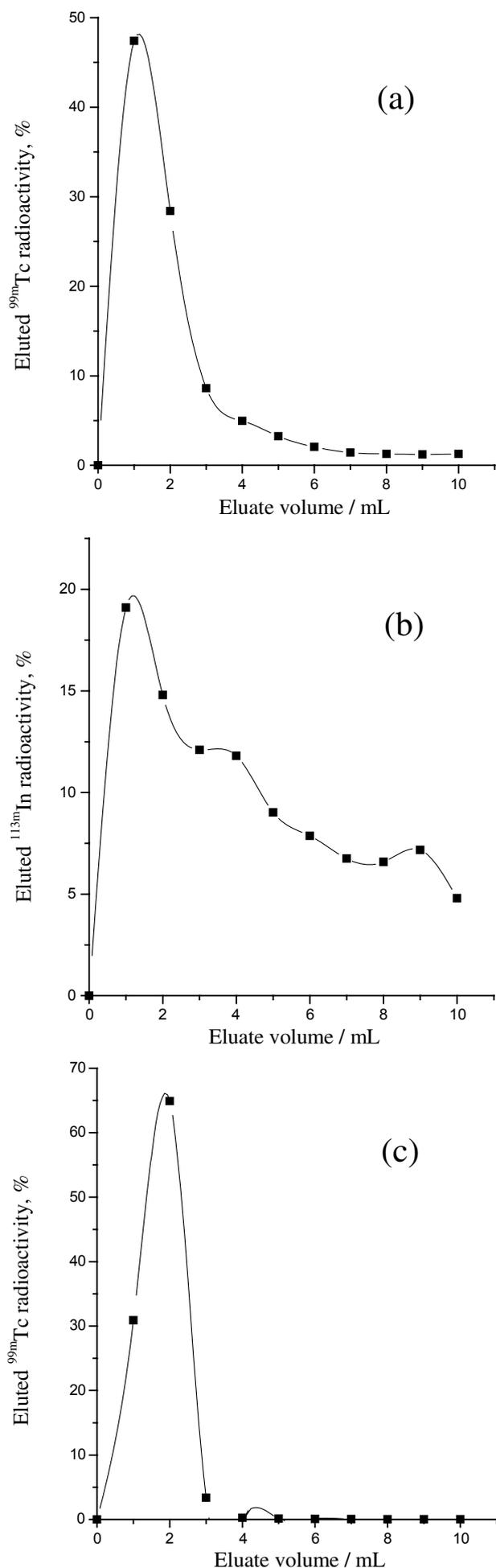


Figure 7. Typical elution profiles of (a) ^{99m}Tc and (b) ^{113m}In eluted from 6-WCe column, and (c) ^{99m}Tc from alumina-column filter with 10 mL of 0.9% NaCl solution.

whereas 0.8% of it was distributed in the last 7 mL of the eluate. To be more concentrated, ^{99m}Tc could be eluted from the alumina-column filter with only 3 mL of 0.9% NaOH solution, i.e. in this case the total ^{99m}Tc eluate volume was 13 mL. Radiochemical purity of the eluted ^{99m}Tc was $96.9 \pm 1.0\%$ (as $^{99m}\text{TcO}_4^-$) with R_f -value of ~ 0.67 .⁵⁸ Before using the alumina-column filter, ^{99m}Tc eluates were found to contain ≤ 1.4 ppm W. After using the alumina column they were found to contain ≤ 2.0 ppm Al and no tungsten was detected. In both cases, no cerium was detected. Such levels of tungsten and aluminum are acceptable for nuclear medicine applications.^{59,62} pH value of the ^{99m}Tc eluate from 6-WCe increased gradually from 3 to 4.3. After using the alumina-column filter, pH value of the ^{99m}Tc eluate was raised to 6.4 ± 1.1 .

3.6. Elution of ^{113m}In . After 60-d period (during which ^{99}Mo was practically completely decayed), the 6-WCe column was conditioned for ^{113m}In elution with 20 mL of 0.1 M HCl. After 18 h, the column was eluted with 10 mL of 0.1 M HCl. Figure 8 shows the γ -ray spectra of 6-WCe column loaded with ^{99}Mo and ^{113}Sn (after practical complete decay of ^{99}Mo) (a) before and (b) after elution of ^{113m}In by passing 10 mL of 0.1 M HCl solution, and (c) ^{113m}In eluate. 0.1 M HCl solution was chosen for elution of ^{113m}In because, according to Figure 2, the highest separation factor was obtained at pH 1; $\alpha = (K_d)_{\text{Sn}} / (K_d)_{\text{In}} = 87 \pm 22$. As radiometrically indicated, elution yield of ^{113m}In was found to be $62.2 \pm 3.7\%$ with a radionuclidic purity of $\geq 99.99\%$. Figure 9 shows a typical elution profile of ^{113m}In from 6-WCe column, after decay of ^{99}Mo , with 10 mL of 0.1 M HCl. According to Figure 9, a sharp elution peak was obtained; 72.6% of the ^{113m}In eluted from the 6-WCe was concentrated in the first 3 mL of the eluate, with a maximum value of 39.6% at 2 mL, while 60.4% of it was distributed in the last 7 mL of the eluate forming a long tail. Thus, it is clear that, the chemical composition of the eluent has an obvious effect on the ^{113m}In elution yield; 0.5 ± 0.3 and $62.2 \pm 3.7\%$ for 0.9% NaCl and 0.1 M HCl solutions, respectively, and on the sharpness of the elution peak, compare Figures 7 (b) and 9. Radiochemical purity of the eluted ^{113m}In was $88.4 \pm 2.5\%$ (as $^{113m}\text{In}^{3+}$) with R_f -value of ~ 0.70 .⁶³ ^{113m}In eluates were found to contain ≤ 0.5 ppm of tungsten, whereas no cerium could be detected. pH value of the ^{113m}In eluates was ~ 1 .

3.7. Simultaneous elution of ^{99m}Tc and ^{113m}In . Otherwise, trials have been carried out, with more or less identical system, to attain eluates of a gradient $\%^{99m}\text{Tc} / \%^{113m}\text{In}$ ratios, by using 0.9% NaCl–HCl eluents of different pH values. However, $\%^{99m}\text{Tc} / \%^{113m}\text{In}$ ratio in eluates depends also on the initial radioactivities of ^{99}Mo and ^{113}Sn loaded onto the 6-WCe column and time of elution, since ^{99}Mo decays faster than ^{113}Sn . These mixed eluates were then passed through a HZO column (pre-conditioned with 0.9% NaCl). Then, ^{99m}Tc and ^{113m}In were separately eluted from HZO column with 10 mL of 0.9% NaCl solution and 15 mL of 0.1 M HCl solution, respectively. It is worth mentioning that no ^{113m}In could be eluted from HZO with HCl eluents of $\text{pH} \geq 2$.²⁵ In addition, HZO was used in this system instead of alumina because it is difficult to consistently elute ^{113m}In from alumina.²³ However, promising results have been obtained from these trials, but more investigations should be performed to obtain systematic results. The ^{99m}Tc and ^{113m}In eluates obtained in these trials were of highly acceptable radionuclidic, and radiochemical purities. In addition, no W, Ce, or Zr chemical impurities were detected. Thus, the simultaneous elution of ^{99m}Tc and ^{113m}In from 6-WCe column and then separation of them from each other using a HZO column may have useful applications in dual isotope imaging.⁸ After decay of ^{99}Mo , ^{113m}In could be directly eluted from 6-WCe column. The ^{113m}In eluted after long decay times will have low radioactivity but still has important applications in crude oil industry.⁷ This may lead to a suggestion that the dual radioisotope generator may be utilized in such industrial applications after decay of

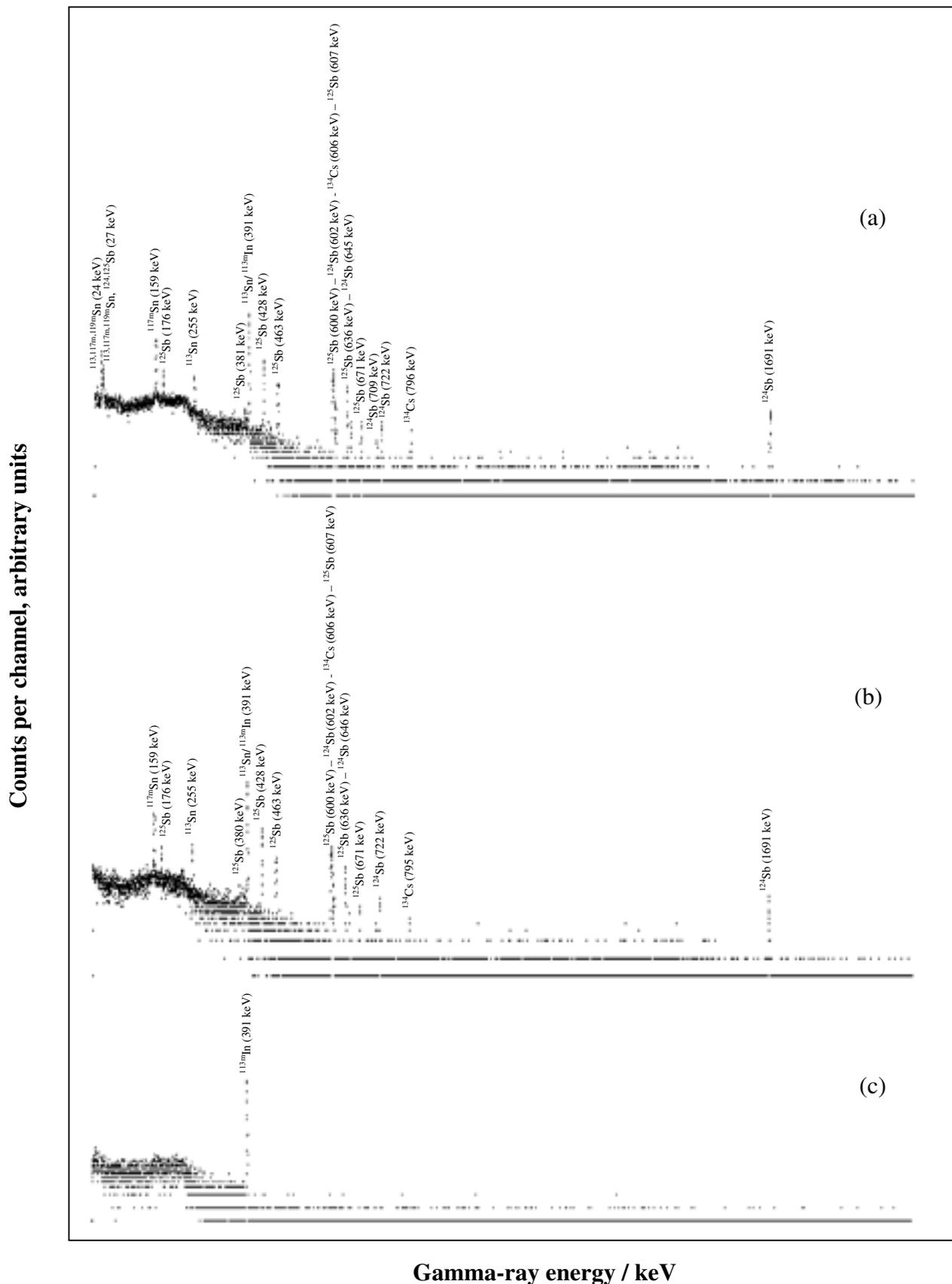


Figure 8. Gamma-ray spectra of 6-WCe column loaded with ^{99}Mo and ^{113}Sn (after practical complete decay of ^{99}Mo) (a) before and (b) after elution of $^{113\text{m}}\text{In}$ by passing 10 mL of 0.1 M HCl solution, and (c) $^{113\text{m}}\text{In}$ eluate.

^{99}Mo instead of sending it directly to the waste.

Figure 10 shows a sketch of a suggested commercial system for $^{99}\text{Mo}/^{99\text{m}}\text{Tc}-^{113}\text{Sn}/^{113\text{m}}\text{In}$ dual radioisotope generator, from which $^{99\text{m}}\text{Tc}$ and/or $^{113\text{m}}\text{In}$ can be eluted by carrying out the proper elution process using the suitable inlets and outlets, which should be clearly labeled to avoid mishandling. For the

dual radioisotope generator, a lead shield with adequate dimensions for containing a radioactivity of e.g. 27.75 GB of ^{99}Mo can be used to contain both of this radioactivity of ^{99}Mo and an equal radioactivity of ^{113}Sn .⁶⁴ This is due to the lower-energy and lower-abundance of γ -rays of ^{113}Sn than those of ^{99}Mo .¹

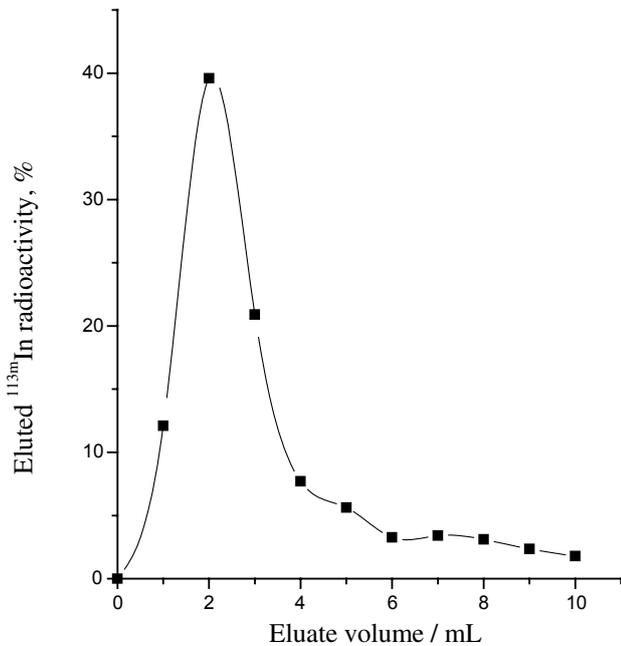


Figure 9. A typical elution profile of ^{113m}In from 6-WCe column, after decay of ^{99}Mo , with 10 mL of 0.1 M HCl

4. Conclusion

A radiochemical procedure was investigated for the preparation of a dual radioisotope generator based on a chromatographic column of 6-WCe inorganic sorbent loaded with ^{99}Mo and ^{113}Sn , and eluted to produce ^{99m}Tc and ^{113m}In subsequently with high radionuclidic, radiochemical, and chemical purities. On the other hand, trials of simultaneous elution of ^{99m}Tc and ^{113m}In from 6-WCe column have been carried out producing eluates of different $\%^{99m}\text{Tc}/\%^{113m}\text{In}$ ratios, which were then passed through a HZO column to separate ^{99m}Tc and ^{113m}In from each other with highly acceptable purities, which may have a special importance in some medical applications (dual isotope imaging).⁸ Furthermore, since the idea of the dual radioisotope generator is the containment of two radioisotope generators in one system, it may lead to saving the shielding and, consequently, shipment costs in addition to minimization of the volume of the produced waste as a final result.

Nevertheless, the dual radioisotope generator system presented by the present work may be considered as mid-stage of development and further investigations should be performed with the system of simultaneous elution of ^{99m}Tc and ^{113m}In from 6-WCe to obtain more real applicable dual radioisotope generator of this type, or in other words to attain (i) more systematic results for ^{99m}Tc and ^{113m}In elution yields, (ii) systems

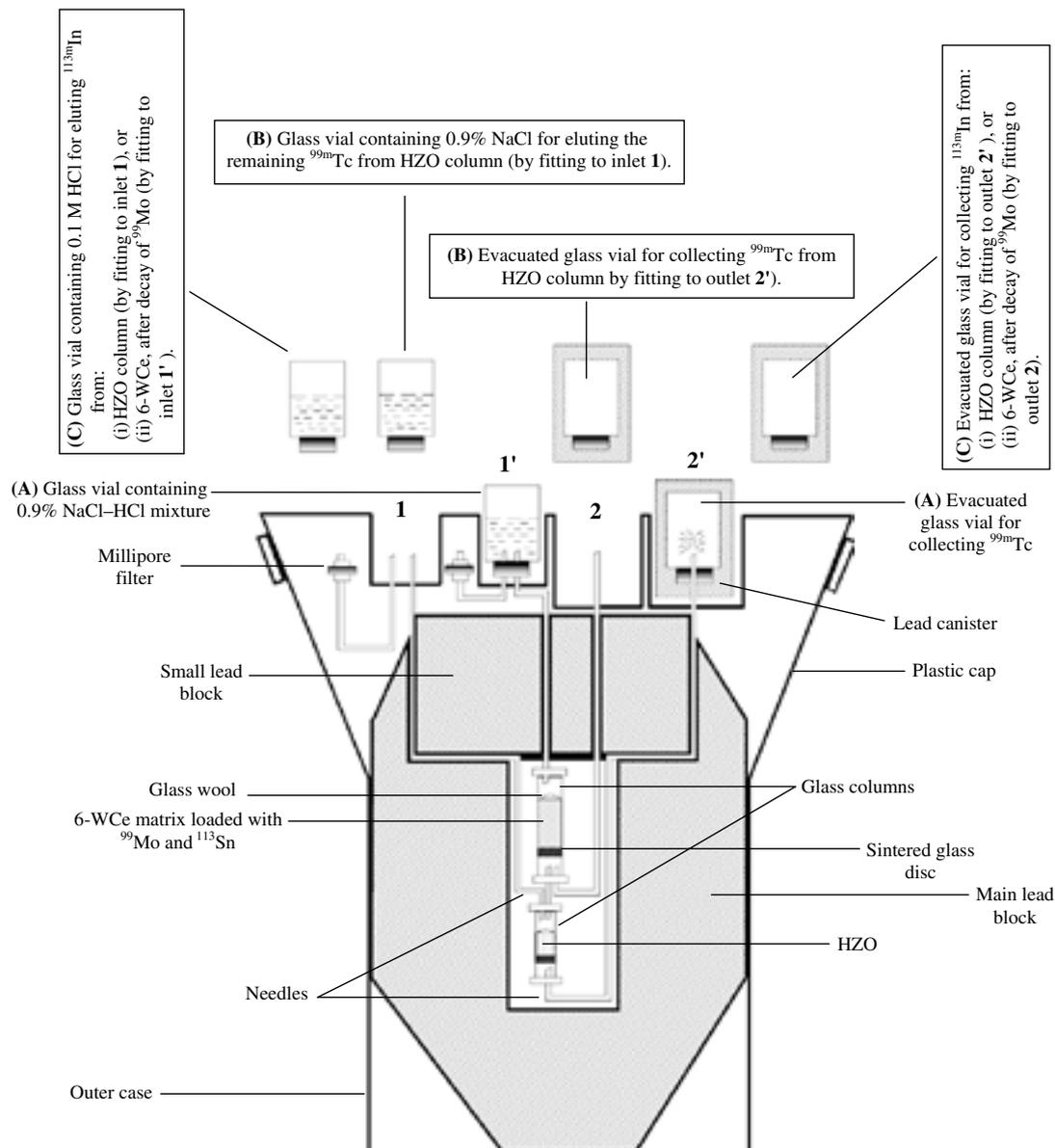


Figure 10. A sketch of a suggested commercial system for $^{99}\text{Mo}/^{99m}\text{Tc}-^{113}\text{Sn}/^{113m}\text{In}$ dual radioisotope generator used for eluting (i) ^{99m}Tc and ^{113m}In simultaneously from 6-WCe column (and separating both of them from each other using HZO column) and (ii) ^{113m}In from 6-WCe column after decay of ^{99}Mo .

with higher radioactivities such as those used in commercial scales, and (iii) simpler systems with easier and fewer steps for elution operations.

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