Review

Determination of Cs-137 in environmental water by ion-exchange chromatography

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Abstract

Methods of Cs-137 determination employing ion-exchange concentration in environmental waters such as seawater and river water have been reviewed. Ammonium molybdophosphate (AMP) is the most used inorganic ion exchanger for the determination of cesium in water. Since AMP could be obtained only in the form of fine crystals, it was difficult to use it in the columns for separation and concentration of Cs-137. Columns with favorable flow-rates, however, could be prepared by precipitating AMP into a resinous structure. Another inorganic ion exchanger, potassium cobalt ferrocyanide (KCFC), was also successfully used for rapid, selective and quantitative concentration of radioactive cesium from neutral, acidic and basic solutions. AMP, KCFC and copper hexacyanoferrate(II) precipitated on silica granules and anion-exchange resins were found superior for concentration of Cs-137 by column method. Recent developments in analytical technology such as application of ion chromatography in the determination of Cs-137 seems promising. Cyclic voltammetry using a $NiFe(CN)_6^{2-}$ derivatized nickel working electrode may be used for the determination of total concentration of cesium in surface waters.

Keywords: Reviews; Water analysis; Environmental analysis; Ion exchangers; Cyclic voltammetry; Caesium-137; Ammonium molybdophosphate; Potassium cobalt hexacyanoferrate

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1. Introduction

1.1. Environmental water pollution

Although industrialization is good for human kind, its rapid growth has created a great risk of water contamination as wastes generated from various industries normally end up in water supplies such as groundwater, rivers, lakes and streams. The use of various pesticides on agricultural lands and home gardens also contribute to water pollution via runoff.

Another source of water contamination is the release of radioactive elements into the atmosphere by the testing of nuclear weapons. Accidents involving nuclear reactors also spread radioactive elements in the atmosphere. One of the significant components of both fallouts from weapons testing and releases from nuclear operations is the radionuclide cesium-137.

Radionuclides differ from other nuclei in that they emit ionizing radiations which can damage living organisms by initiating harmful chemical reactions in tissues. It takes ten half lives for the loss of 99.9% of the activity of a radionuclide. If the half life of a radioactive element is very short (seconds or minutes), no harm will be done since most of the material will have decayed before its entry into the food chain or water supply. Similarly if the half life of a radioisotope is measured in millions of years, no significant amount of radiation will be generated during the lifetime of the subject who has ingested it. However, a radioelement with a half life of 30 years will generate significant radiations [1] and will be harmful to the living tissues depending upon the amount adsorbed. Cesium-137 with a half life of 30.1 years is one such gamma-emitting radionuclide.

Atmospheric contaminants reach the ground by wet and/or dry deposition processes and are added to our water supplies. As the water flows through rivers, lakes and streams, the contaminants add up and normally end up in the ocean. Radioactive cesium may also reach seawater from naval or marine reactors and from stationary reactors on rivers or estuaries. However, the concentration of dissolved contaminants in the ocean rises slowly because of its large volume.

1.2. Need for the determination of pollutants in environmental waters

Although nature has the ability to clean the air and water, due to increased population, new life-styles, and the growth of industries, the rate of pollution often exceeds the rate of natural cleaning. Polluted water can cause disease in humans and increase the costs of production in industries. This necessitated the cleaning of water by artificial means. The treatment with artificial means requires complete characterization of water samples for different pollutants in order to develop a cost-effective plan.

1.3. Determination of Cs-137 in environmental waters

In the present-day World, atmospheric testing of nuclear weapons and nuclear reactor accidents is not uncommon. These activities have created a great risk of frequent release of small amounts of cesium-137 into environmental waters. Being a strong gamma-radiation emitting isotope, the determination of Cs-137 in environmental waters, such as seawater and riverwater, is of considerable importance. Due to this reason, since the advent of nuclear technology, methods for determination of stable and radioactive cesium (Cs-137) in environmental waters are developed. The determination of cesium concentration

in these waters is complicated due to its very low concentration, ranging at $(2.9–6.5) \cdot 10^{-9}$ M. This trace concentration of cesium is present with very large concentrations of sodium, potassium, magnesium, calcium, chloride, sulfate and bicarbonate, which together constitute 99.7% of the total solids in sea, surface and ground waters [2,3]. The principal problem in the determination of Cs-137 in environmental waters therefore is the separation and concentration of its submicrogram quantities from decigram or gram quantities of common alkali metals from a large volume of water.

Preconcentration of cesium is normally carried out on cesium-selective ion exchangers. Therefore, during the last 35 years, a large number of ion exchangers has been investigated for the selective concentration and separation of Cs-137 from other radionuclides which could interfere with subsequent gamma-ray spectrometric determination. These ion exchangers include organic resins, liquid ion exchangers (solvent extractants) and inorganic ion exchangers. Inorganic cation-exchange materials are probably the most important ion exchangers, not only for the isolation of this radionuclide, but also as a general means of separating the heavy alkali metal ions from each other and from virtually all other elements. Moreover, most inorganic ion exchangers have good chemical stability in the presence of nuclear radiation, a property that is not possessed by organic resins which suffer from partial degradation when exposed to nuclear radiation.

This review reports on the methods of Cs-137 determinations in environmental waters, such as natural and seawater, using ion-exchange chromatography for concentration and separation steps. Also reported are the references related to the preparation of different cesium-selective ion exchangers including new compounds showing high selectivity for cesium. Recent developments in the methodology are critically discussed.

2. Ion exchangers showing high selectivity for cesium

A large number of ion-exchange and solvent-extraction systems have been investigated to achieve selective sorption/concentration of cesium from aqueous solutions.

2.1. Organic ion exchangers

Separation of alkali metals can be achieved by chromatography on cation-exchange resins [4]. The sorption studies for different alkali metal ions on strongly acid cation-exchange resins containing sulphonic acid groups, e.g., Dowex-50 indicated selectivity for cesium [5,6] and other alkali metals in the order Li<Na<K<Rb<Cs. Although due to the small difference in their selectivity Dowex-50 could be used for the separation of lithium, sodium, potassium, rubidium and cesium ions from solutions in which their concentrations were of the same order, a complete separation of small concentration of cesium from large concentration of sodium was not possible on this exchanger as the separation factor between Na^+ and Cs^+ was not large enough. Among the organic resins investigated for selective sorption of Cs-137, bifunctional resins containing phenol groups in addition to sulphonic groups, e.g., Duolite C-3 or Diaion SK1 revealed specific selectivity for cesium from alkaline solutions [7–12]. This specific adsorption of cesium on these ion exchangers was suggested to be due to the complex formation between Cs^+ and phenol groups of the resins. The adsorption on both types of resins was used to separate the heavy alkali metals from each other and from alkaline earth metals.

Early references on solvent extraction of cesium can be found in a paper by Koyama et al. [13] in which they reported quantitative extraction of Cs-137 by the complex anion, $[Cr(NH_2C_6H_5)_2(NCS)_4]^-$, in nitrobenzene at pH 2–10. The method was applied to concentrate Cs-137 from a natural mixture of fission products and cooling water from a nuclear reactor. For the extraction of cesium from these samples, the pH was adjusted to 8 because slightly basic pH was necessary for the masking of polyvalent cations by EDTA. Radiocesium extracted or ion-paired with $[Cr(NH_2C_6H_5)_2(NCS)_4]^-$ in non-aqueous media was back-extracted into the aqueous phase by shaking the organic phase with 6 M HCl for its quantification. Schulz and Bray [14] reviewed the literature on solvent extraction of Cs-137 from highly acidic solutions. In a recent paper McDowell et al. [15] reported on the selective extraction of cesium from acidic nitrate solutions with didodecylnaphthalenesulfonic acid in the presence of bis(tert.-butylbenzo)-21crown-7.

2.2. Inorganic ion exchangers

The use of inorganic compounds for ion-exchange separation of radiocesium gained popularity on account of their superior resistance to radiation and usually higher thermal stability as compared to organic ion-exchange resins. Some inorganic ion exchangers also showed specific selectivity for cesium. Important examples of inorganic ion exchangers which can be used for selective concentration of Cs-137 are dodecaheteropolyacid salts of molybdenum and tungsten, such as ammonium 12-molybdophosphate commonly known as AMP and ammonium 12-tungstophosphate commonly known as ATP, and complex cyanides, such as insoluble hexacyanoferrate(II) and hexacyanoferrate(III) salts of transition metals. Recently other ion exchangers showing high selectivity for cesium are also reported. These include zeolites, micas, hydroxy oxides of pentavalent metals, and acid salts (such as silicates, phosphates, molybdates, tungstates etc.) of group III and IV metals.

The early work on inorganic ion exchangers was reviewed by C.B. Amphlett [16], Pekarek and Marhol [17], Vesely and Pekarek [18,19], Abe [20], Clearfield et al. [21], and Clearfield [22]. Inorganic ion-exchange materials have not been used as extensively in analytical chemistry as organic resins, especially for the analysis of inorganic ions. However, ion-exchange concentration of Cs-137 during its determination in environmental waters is carried out mostly, if not exclusively, on inorganic ion exchangers.

2.2.1. Heteropolyacid salts

Although a large number of insoluble salts of dodecaheteropolyacids are studied for the purpose of selective concentration of cesium from aqueous solutions, ammonium dodecamolybdophosphate (AMP) is the most extensively investigated ion exchanger. Ion-exchange properties of AMP [$(NH_4)_3Mo_{12}O_{40} \cdot xH_2O$] for cesium were discovered by Smit et al. [23,24]. Since then this exchanger has been widely used for the determination of cesium in environmental samples. The selectivity of AMP for cesium is considerably higher than conventional organic resins (Table 1). The distribution coefficient (K_d) value for cesium on AMP is almost 100 times

Table 1
Distribution coefficients of alkali metals in 0.1 M ammonium nitrate on AMP and Dionex-50 in NH_4^+ form (reproduced from Ref. [24])

Cation exchanger	K_d			
	Na^+	K^+	Rb^+	Cs^+
Dowex-50 (NH_4^+ form)	26	46	52	62
AMP (air dried)	<1	3.4	230	6000

higher than on Dowex-50 in ammonium form [23]. These results also showed a very large value of separation factor for Cs^+/Na^+ ion pair at 6000 or greater on AMP. The separation factor for Cs^+/Na^+ ion pair was only 2.4 on Dowex-50. The large separation factor on AMP suggests that this exchanger can be used for selective concentration of Cs^+ ions in the presence of a very large excess of sodium. Due to the small separation factor between Cs^+/Na^+ ion pair, Dowex-50 ion exchanger could not be used for the preconcentration of cesium in the presence of a large concentration of sodium ions.

AMP contains exchangeable NH_4^+ ions which can be exchanged for Cs^+ and other heavy alkali metal cations such as Rb^+ and K^+. However, due to its very high affinity, cesium ions can be adsorbed quantitatively from the solutions containing large concentrations of potassium and rubidium. For example, presence of potassium ions in solution saturated with potassium salt could not stop the uptake of cesium ions on AMP. At acidic pH values (1 or lower), the exchange of cesium on AMP was reported to be very rapid and was not significantly affected by the high ionic strength of the solution. Even at neutral (or close to neutral) pH values such as in seawater, a large distribution coefficient for cesium (1500) was reported [25,26]. High selectivity and rapid sorption rate of cesium on AMP was the most important advantage of this exchanger over the organic ion-exchange resins for its use in the determination of Cs-137 in environmental waters. Other advantages included its stability in the presence of nuclear radiation and easy availability at low cost. AMP can also be easily prepared in the laboratory [27-29].

The salts of various other dodecaheteropolyacids also showed similar sorption properties as AMP. The ones which are most frequently used for the isolation

of cesium and other heavy alkali metals, such as rubidium and francium, from acid solutions are the salts of dodecatungstophosphoric acid [30–33] and dodecatungstosilicic acid [11,34–36]. Thallium(I) dodecatungstophosphate was also found to be specifically selective for cesium [31].

2.2.2. Insoluble hexacyanoferrate(II) salts of transition metals

Insoluble salts of transition metals with hexacyanoferrate(II) can incorporate alkali metal ions into their crystal lattices. The alkali metals on hexacyanoferrate(II) ion exchangers are generally adsorbed with increasing strength in the order Li< Na<K<Rb<Cs. This sorption behavior is similar to that of heteropolyacid ion exchangers. Like AMP and other heteropolyacid salts, many hexacyanoferrate(II) ion exchangers also showed specific selectivity for cesium. These included hexacyanoferrates(II) of nickel(II) [37], zinc(II) [37], iron(III) [38,39], tungsten(VI) [40], cobalt(II) [41–44], and molybdenum(VI) [45], ferrocyanide-bentonite [46], and vanadium ferrocyanide [47].

Among these compounds potassium hexacyanocobalt(II)ferrate(II) [42,48,49], which can be prepared in granular form, is reported to be highly selective absorbent for cesium ions. This exchanger, commonly known as KCFC, could specifically concentrate cesium from large volumes of aqueous samples at high flow-rates. No pretreatment was necessary for most samples and the exchange of cesium was not affected by sample pH. The uptake of cesium on this exchanger is reported to be taken place by ion-exchange mechanism.

Zinc ferrocyanide(ZnFO) is another ion exchanger reported to be selective for cesium. This exchanger can also be prepared in granular form suitable for column use. Experimental work was carried out to demonstrate its utility in the concentration of Cs-137 from aqueous samples [37].

Krtil [40] studied the sorption of Cs-137 and Rb-86 on tungsten ferrocyanide. Selectivity coefficients for these cations were determined under static conditions. In other studies, freshly prepared $Cu_2Fe(CN)_6$ was used for sorption of Cs-134 and Cs-137 [50]. Vanadyl ferrocyanide [47] was reported as useful ion exchanger for selective isolation of

Cs-137 from strongly acidic solutions of fission products.

The affinities of insoluble ferrocyanides of Fe(III), Cu(II), Zn(II), Ni(II), and Co(II) for alkali metal ions was studied by Dolezal and Kourim [51]. They found that the total amount of the alkali metal ions incorporated in the precipitates increased from sodium to cesium. In another paper, Kourim et al. [52] reported the properties of various transition metal ferrocyanides as ion exchangers for cesium. These authors concluded that zinc(II) and copper(II) compounds were the most promising materials for column operation among the ferrocyanides of zinc(II), copper(II), nickel(II), cobalt(II), iron(III), lead(II), cadmium(II), bismuth(III) and silver(I).

The product 'ferrocyanide molybdate' (FeMo) also possessed attractive ion-exchange properties [53] in regard to selective separation and recovery of cesium from highly radioactive solutions. Equilibration of the exchanger with aqueous solutions containing mono-, bi- and tri-valent cations showed that cesium was preferred to all other cations studied.

The preparation and properties of sodium–copper cyanoferrate(II) (NaCuFC) for the removal of cesium from nitric acid solution was reported by Shahbandeh and Streat [54]. The properties of this adsorbent depended greatly on the concentration and volume ratio of the reagents used in its preparation. The sorption of cesium from different aqueous solutions was conducted in a series of experiments. In pure water NaCuFC was found to be an effective scavenger for cesium and the distribution coefficient of cesium increased with increasing pH up to 10.5. In the presence of competing ions, such as sodium or magnesium, the distribution coefficients of cesium on NaCuFC were greatly reduced. Optimal sorption under these conditions occurred at a pH of about 2.

2.2.3. Insoluble hexacyanoferrate(III) salts of transition metals

Sorption behavior of about 50 ions in nitric acid medium on zinc(II) hexacyanoferrate(III) (ZFiC) was studied by Valentini et al. [55] by batch equilibration. ZFiC was formed by the oxidation of zinc(II) hexacyanoferrate(II) (ZFoC) in nitric acid solutions of molarity greater than 0.1 M. ZFoC, prepared in granular form, was found suitable for column separation of cesium from other cations.

Jain et al. [56,57] reported the preparation and exchange properties of chromium(III) hexacyanoferrate(III) gel (CFiC). This exchanger showed specific selectivity for monovalent cations. Among the monovalent cations, high selectivity was obtained for Ag^+, Cs^+, Tl^+ and Rb^+. The exchanger was prepared in the form of hard granules suitable for column operation. Adsorption of cesium was not significantly affected by the presence of up to 2 M Na^+ ions. Cesium, adsorbed on the columns, could be eluted with small amounts of 10 M nitric acid. These properties suggest that CFiC can be used for selective concentration and separation of cesium from seawater.

Copper(II) hexacyanoferrate(III), which can be converted into granular form suitable for column operation, was also prepared [58]. This exchanger showed very high selectivity for cesium over mono-, di-, tri- and tetra-valent metal ions. Separation of cesium from a number of other metal ions was achieved on the column of this exchanger.

A comparison of sorption studies of cesium on hexacyanoferrate(III) salts of Cr(III) [56], Cu(II) [58], Co(II) [59,60], Sn(II) [61], and Zr(IV) [62], indicated high selectivity for cesium only on chromium and copper compounds [63]. These studies [63] which were aimed at using the copper(II) hexacyanoferrate(III) ion exchanger for the selective recovery of cesium ions from nuclear waste showed 95% recovery from simulated waste.

2.2.4. Zeolites

Wingefors et al. [64] reported the performance and use of mordenite for the sorption of cesium and other fission products from an acidic radioactive waste solution. A complete removal of cesium was achieved by the use of mordenite columns, as no cesium could be detected in the effluent. Very little adsorption of other fission products was observed. In spite of the acidic nature of the feed solution, no signs of degradation of the zeolite structure were noticed. Mordenite columns could thus be used to isolate cesium from acidic radioactive solutions. The selective sorption of cesium and strontium from high-activity-level water was also studied on various other zeolites [65]. The rate of adsorption of cesium and strontium increased with the decrease in zeolite particle size. An uptake of close to 100% was

observed for cesium and strontium after shaking for 5 and 10 h, respectively.

2.2.5. Hydrous oxides

Layered vanadium pentoxide gels, analogous to montmorillonite-layered silicate, could be synthesized under hydrothermal conditions at 200°C [66]. This ion exchanger exhibited high selectivity for cesium ions in the presence of highly concentrated solutions containing Li^+, Na^+, K^+, Mg^{2+}, Ca^{2+}, Ba^{2+}, and Sr^{2+}. Cesium selectivity of this exchanger could be useful in the separation of Cs-137 from radioactive waste solutions or naturally occurring brines such as seawater.

2.2.6. Micas

The cation selectivity of Na-substituted fluor-micas, which are swellable in water, was investigated by Miyake et al. [67]. In this paper the authors report the discovery of an excellent Cs^+ ion sieve effect of Na-substituted hectorite (NaH) with no dependence on the concentration of Cs^+ ions. The Cs^+ ion selectivities of Na-substituted taeniolite (NaT) and Na-substituted tetrasilicic mica (NaTS) are also determined and compared with that of NaH. The basic studies suggest that NaH can be utilized in the separation and immobilization of Cs^+ ions from solutions containing Na^+, K^+, and Cs^+ ions.

Hydrated sodium phlogopite mica made by careful low-temperature leaching, showed extremely high selectivity for cesium [68]. On the basis of high selectivity of this exchanger for cesium from concentrated solutions containing Na^+ or Ca^{2+}, it was suggested that the exchanger could be used in the preconcentration of cesium from environmental waters.

2.2.7. Acid salts of group(III) and (IV) metals

Acid salts of zirconium showed high selectivity for heavy alkali metals in acid solutions. Zirconium phosphate [69–72], zirconium molybdate [73], and zirconium tungstate [74] were used for the isolation of cesium-137 [71,73,74]] and to separate cesium from rubidium [69,74]. These separations can be performed on columns or on filter papers impreg-

nated with these materials [70]. Similar ion-exchange properties are also shown by hydrated titanium dioxide in ammonium form [73], stannic phosphate [75], and clay minerals [76].

Betteridge and Stradling [77] reported a glassy chromium polyphosphate ion exchanger which showed specific selectivity for monovalent cations. The order of selectivity amongst monovalent ions was Cs>Rb>K>Na>H. The uptake of potassium, rubidium and cesium ions at pH 2 and 3 was not affected by manyfold molar excess of Ni(II), Co(II), Mn(II), Cd(II), Zn(II), Ca(II), Sr(II), Mg(II), Fe(III), Cr(III) ions. This ion exchanger exhibited no affinity for multivalent ions. Another paper by the same authors reported [78] batch and column ion-exchange reactions of alkali metals with chromium tripolyphosphate exchanger. The exchanger was found suitable for column chromatography due to its good mechanical and chemical stability.

Crystalline γ-zirconium phosphate (γ-ZrP) is reported as a highly selective cesium-ion sieve by Komarneni and Roy [79]. The exchanger may be used to separate Cs-137 from circulating (cooling) water in nuclear reactors. High selectivity of this exchanger for Cs-137 can also be utilized for pre-concentration of this radioisotope present at pg ml^{-1} in the presence of very large concentrations of sodium.

Recently Clearfield [80] reported the synthesis and ion-exchange properties of new layered zirconium compounds with different amounts of $(HPO_4)^{2-}$ groups varying from 1 to 4. These new compounds showed very high selectivity for cesium, as the K_d values for cesium ranged from 65 to 3347. Because of their very low selectivity (K_d values for sodium were <10) for sodium, these compounds can be used for the preconcentration of radiocesium from environmental waters.

3. Determination of Cs-137 in seawater

Various chromatographic systems were developed to concentrate and isolate cesium using ion-exchange resins, inorganic exchangers, as well as solvent extraction methods. Several such methods are presented in a book by Korkisch [4].

3.1. Determination via preconcentration on AMP and other heteropolyacid salts ion exchangers

AMP, since it was first reported [23], has been used for the determination of Cs-137 in a variety of materials including natural and sea waters [81–84]. Many procedures such as batch adsorption and concentration on columns have been reported [24,85–88] A batch adsorption method has also been used to determine inactive cesium in seawater [89]. The accuracy of cesium determination was tested by the recovery of known amounts of cesium added to the water samples. These results indicated good accuracy of cesium determination as the recovery of cesium ranged between 94 and 99%.

Although, extensive use of AMP as a cation exchanger to concentrate Cs-137 in environmental waters has been made, because of its microcrystalline form, flow-rates on its column were low. In some cases, especially, in large-scale operations a low cesium recovery of 70–80% has been reported from seawater [81,84]. Because the column method was more efficient and convenient to concentrate cesium from large volumes of water, efforts were made to prepare AMP columns with the aid of different supports which could provide higher flow-rates. It is reported that columns made by the mixture of AMP with Asbestos fiber [24,90] and filter paper pulp [31] generated higher flow-rates than AMP alone. Preparation of AMP with coarse particles, suitable for column use, had also been reported [91]. AMP with rugged particles, which provided desired high flow-rates of seawater through its columns, was prepared by direct precipitation of AMP into the IRA-900 resinous structure [92].

Cunha and Sakai [92], who prepared granular AMP-IRA-900 resin, reported selective preconcentration and determination of Cs-137 in waters in the presence of strontium-90 and potassium-40 by column method. In this work, the water sample was passed through the resin, which retained cesium. Cesium was later eluted with 1 M sodium hydroxide and dissolved AMP was precipitated by acidifying the solution. These results showed good reproducibility and recovery of cesium. A complete decontamination from strontium-90 and potassium-40 was also obtained. The analysis of cesium using AMP on chromatographic columns gave a better recovery of

cesium in comparison with coprecipitation of cesium with AMP. According to these authors AMP-IRA-900 exchanger was found suitable for the determination of cesium in seawater samples.

A rapid and precise method for the determination of radiocesium in seawater with the aid of AMP-Amberlite XAD-7 resin (prepared by direct precipitation of AMP into the resinous structure of Amberlite XAD-7 resin) had been reported by Nakaoka et al. [85]. Radiocesium in seawater was collected on this resin by the batch method. Elution of adsorbed cesium from the ion exchanger was approximately 100%. The concentration of Cs-137 in natural seawater, determined by this method, ranged 0.13–0.16 $pC l^{-1}$. The analysis of one sample could be completed in 3 h.

Preparation of AMP supported in silica gel and its application in the determination of radioactive cesium in seawater has been reported by Terada et al. [87].

Among other heteropolyacid salts tungstosilicic acid was used for separation and concentration of cesium from seawater [11,34].

3.2. Determination via preconcentration on hexacyanoferrate(II) ion exchangers

Shamaev and Chudinovskich [93] reported pre-concentration and determination of cesium from seawater with nickel(II) hexacyanoferrate(II). Thirty-four samples of seawater taken from different parts of the Atlantic Ocean were analyzed. The cesium concentration in the Atlantic Ocean was reported at 0.74±0.03 $\mu g l^{-1}$. Analyses were done on board of the research ship. The accuracy of the method was verified by standard additions. Total time of the analysis was reported to be 8–10 h. Several parallel determinations were possible; therefore, working time per analysis could be reduced significantly.

Batch adsorption of cesium on nickel ferrocyanide has also been used for the isolation of radioactive cesium from seawater by Mohanrao and Folsom [94]. In this method radioactive cesium, together with microgram amounts of stable cesium naturally present in seawater was co-precipitated with nickel ferrocyanide from a sample of 50 to 200 l. After the

precipitate had settled and the supernatant had been syphoned off, the nickel ferrocyanide was transferred to a pint container and counted in a gamma-ray spectrometer. The influence of various parameters on cesium determination was studied. The simplicity of the method made it convenient for processing samples on board the ship. Thus, precipitates (in pint containers) could be sent to the laboratory for gamma-ray spectrometric analysis in place of samples of 55 gallon (1 gallon is ca. 3.75 l) of seawater.

Inorganic ion exchanger, potassium cobalt ferrocyanide (KCFC), has been used by Boni [41] for rapid, preferential, and quantitative concentration of cesium from neutral, acidic and basic solutions. He reported that concentration of trace quantities of cesium in the presence of large amounts of sodium, calcium and magnesium was possible on KCFC. A method for the determination of radiocesium in seawater and fresh water was developed using a column containing Bio-Rad Celex 100 chelating resin in calcium form and KCFC. The ion-exchange column used for the concentration of cesium from seawater consisted of a 4-inch-long (1 inch is 2.54 cm) polyethylene cylinder as shown in Fig. 1. The column was filled to a height of 1.5 inches with a water slurry of water-washed KCFC supported by a glass wool pad. The remainder of the column was filled with 50 to 100 mesh Bio-Rad Celex 100 chelating resin in calcium form. The function of chelating resin column was to remove interfering radionuclides such as ^{60}Co and ^{65}Zn (Table 2). The specificity of KCFC for cesium enabled rapid concentration of trace quantities of radiocesium directly from large volumes of seawater. The granular form of KCFC (30–60 mesh) allowed a rapid flow-rate for processing 50 gallons or more of sample necessary to obtain the desired concentration levels. Efficiency for the removal of Cs-137 remained greater than 99% up to flow-rates of 10 gallons per hour. However, the removal of other radionuclides by the chelating resin required a flow-rate of 1 gallon per hour for a removal efficiency greater than 95%. A detection limit of 0.07 $pC l^{-1}$ for Cs-137 was obtained using 50 gallons of seawater and a 9×9-inch NaI gamma detector system with a 3×6-inch well.

Frigieri et al. [95] used a column of ammonium hexacyanocobalt ferrate ion exchanger for the determination of the total concentration of cesium in
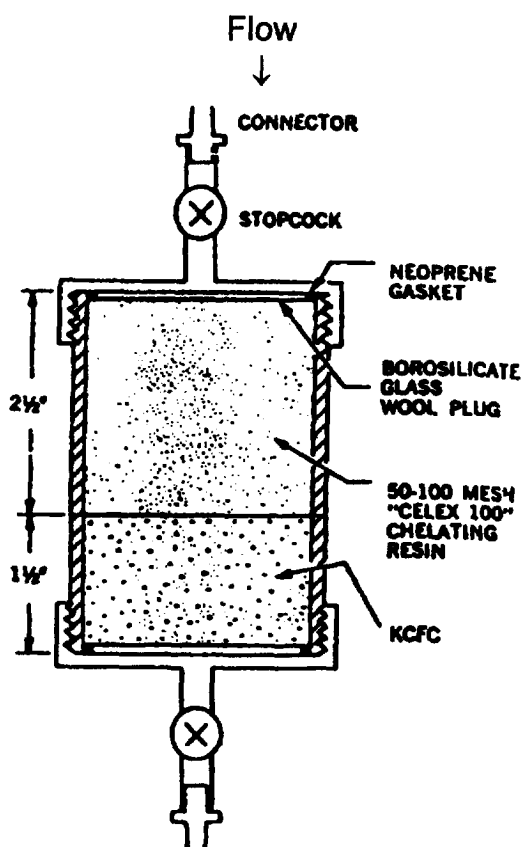
Fig. 1. Dual ion-exchange column used for Cs-137 analysis of seawater. (Reproduced from Ref. [41].)

seawaters by electrothermal atomic absorption spectrometry.

Although as mentioned above, potassium cobalt ferrocyanide (KCFC) was successfully used for the determination of trace concentrations of Cs-137 in

seawater, the method lacked a satisfactory procedure for elution of the adsorbed cesium. This made it impossible to reduce the volume of the counting sample in order to raise the counting efficiency. Moreover, a large amount of exchanger had to be thrown away after only one use. This shortcoming of KCFC inspired researchers to develop hexacyanoferrate(II) ion exchangers suitable for the selective adsorption and elution of Cs-137.

Watari and co-workers [96,97] investigated synthesis of copper ferrocyanide-anion exchange resin and studied the adsorption and desorption of Cs-137 on this resin. They reported that the resin could be used for the concentration of Cs-137 found in seawater. Adsorption of cesium was specific and was entirely due to the ferrocyanide moiety of the resin. This method was more efficient than the coprecipitation method with copper ferrocyanide. The adsorbed Cs-137 was eluted with 6 M nitric acid solution. The method was compared to the AMP method and was found to be simpler for effectively concentrating Cs-137 from large volumes of seawater.

Determination of Cs-137 in seawater by ion-exchange concentration on cobalt hexacyanoferrate(II)-organic anion-exchange resin was also reported [98]. The ion exchanger, cobalt ferrocyanide was prepared in the matrix of an organic anion exchanger AV-16 G. The method was used to determine Cs-137 at three locations in the Atlantic Ocean.

Terada et al. [87] investigated the preparation of KCFC and ammonium hexacyanocobalt ferrate (NCFC) supported on silica gel for the determination of Cs-137 in natural and seawaters. A simple method of preparing KCFC–SiO_2 or NCFC–SiO_2 was reported. NCFC was considered a better material in the

Table 2
Percent retention of Cs-137 and interfering radionuclides on various combinations of dual column containing KCFC in bottom bed (reproduced from Ref. [41])

Sample solvent:	H_2O	H_2O	1 M HCl–0.5 M HF		10 M HCl–0.5 M HF
Top resin bed:	—	Celex 100 (Ca^{2+} form, chelating resin)	–	Dowex 1×8 (anion resin)	Dowex 1×2 (anion resin)
Bottom resin bed:	KCFC	KCFC	KCFC	KCFC	KCFC
Cs^{137}	99	99	99	99	99
$Ru^{103,106}$	75	44	<0.1	<0.1	<0.1
Zr^{95}–Nb^{95}	95	73	<0.1	<0.1	<0.1
Zn^{65}	95	<0.1	95	<0.1	<0.1
Co^{60}	95	<0.1	95	95	<0.1

sense that potassium interference was eliminated by the use of ammonium ion. Cs-137 was almost quantitatively adsorbed from 100 l of seawater on a column containing 10 g exchanger at a flow-rate of 10 l h^{-1}. Addition of cesium carrier enhanced the adsorption yield of Cs-137 on the exchanger. Four surface water samples collected from the Japan Sea were analyzed for their Cs-137 concentration using KCFC–SiO$_2$. The results were compared with AMP precipitated on SiO$_2$ and the co-precipitation method used by Miyake et al. [99].

Ganzerli-Valentini et al. [100] described the preparation of copper hexacyanoferrate(II) supported on silica granules. The material was used for concentrating trace cesium, both stable and radioactive, from seawater with a recovery efficiency of about 94%.

Mann and Casso [101] used a novel approach for in situ extraction of cesium radionuclides from seawater. In this approach, cesium (stable and radioactive) was partially stripped from seawater as it passed in series through twin beds of cupric ferrocyanide-impregnated ion-exchange resin in a cartridge made of PVC pipe fittings. When seawater passed through this cartridge at a constant flow-rate, collection efficiencies of each bed were the same. Procedures for resin preparation, desorption and radiochemical purification of the collected cesium have been described.

4. Determination of Cs-137 in riverwater

Radiocesium in riverwaters is usually present at very low concentrations. This requires a pre-concentration step in its determination from a very large volume of water (50–100 l). Use of ion-exchange columns was therefore recommended for this purpose. Although precipitation [81] and column chromatography [102,103] have both been used, only a small amount of exchanger was sufficient for treating large volumes of water in either case.

Batch adsorption on AMP has been used to determine inactive cesium in river water [89]. The recovery of cesium was between 94 and 99%. Other ion exchangers and precipitation procedures have also been used to determine Cs-137 in river water [104].

Total concentration of cesium in river waters was determined by electrothermal atomic absorption spectrometry after its selective retention on a column of ammonium hexacyanocobalt ferrate ion exchanger [95].

In another study, Watari et al. [105] investigated adsorption of Cs-137 on metal ferrocyanide-anion exchange resin, made by the precipitation of different metal ferrocyanides on an anion-exchange resin matrix. Results showed that Cu(II), Fe(II) and Ni(II) ferrocyanide-anion exchange resins can be used for a rapid quantitative concentration of radiocesium. The authors believed that specific adsorption of cesium from river water was caused by the metal ferrocyanide moiety of the resin.

Ganzerli-Valentini et al. [100] used columns of copper hexacyanoferrate(II) supported on silica granules oxidized to copper hexacyano ferrate(III) for collecting cesium from large volumes of river water. No pretreatment of river water was necessary and the procedure could be used for stripping cesium, either stable or radioactive, from large volumes of water. The elution of cesium from the ion-exchange column was accomplished with 8 M HNO$_3$. Quantitation of eluted cesium was made by gamma-ray and/or atomic spectrometry. According to the authors, elution of adsorbed cesium from copper hexacyano ferrate(III)-silica column was the main advantage of their method, as ion exchangers such as KCFC adsorbed cesium irreversibly [42]. Mean recovery of cesium from river water was reported to be 94%.

5. Recent developments

Cesium can be determined by ion chromatography [106,107], as has been reported in recent publications [63,108–111]. A high detection sensitivity for cesium can be obtained by suppressed ion chromatography as shown in Fig. 2. Recently, Reiffnsthul and Bonn [111], using a liquid scintillation β-counter as detector (in place of a normal conductivity detector), demonstrated the use of ion chromatography for the determination of Cs-137 and Sr-90 in water (Fig. 3). A similar approach was also used by Alfaro et al. [112]. According to Reiffnsthul and Bonn [111] ion chromatography seemed promising
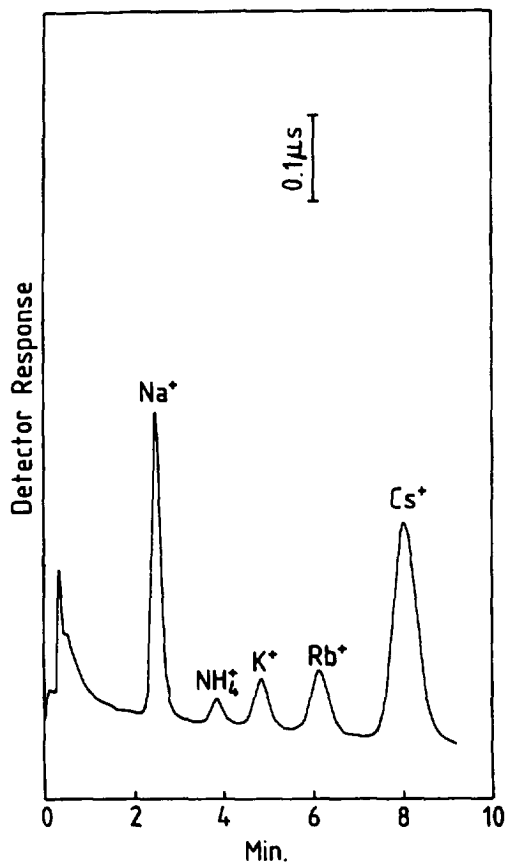
Fig. 2. Suppressed ion chromatogram showing separation of 1 ppm Cs^+ from small concentrations (<1 ppm) of other alkali metal ions and matrix containing Al, Fe and U. (IC conditions included a Dionex CG-1 analytical column, 5.0 mM HCl as eluent at 2 ml min^{-1} flow-rate, 100 μl injection volume and a Dionex 2010 ion chromatograph with conductivity detector). (Reproduced from Ref. [63].)
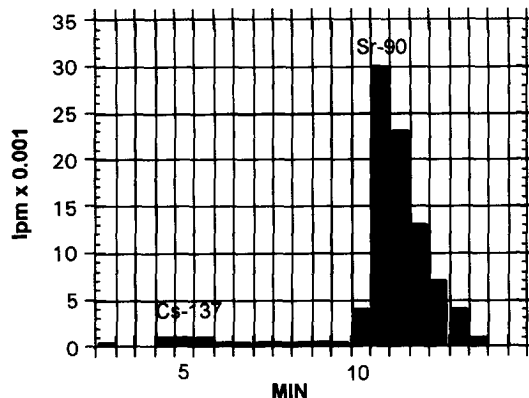

Fig. 3. Ion chromatographic trace analysis of radionuclides, impulses per min (Ipm) versus time. Sample: Cs-137 and Sr-90 in water. Stationary phase, TSK IC cation SW; mobile phase, 3.5 mM ethylenediamine–10 mM citric acid (pH 4.80, adjusted with NaOH); flow-rate, 0.7 ml min^{-1}; detection, β-liquid scintillation counting. (Reproduced from Ref. [111].)

for simple and rapid determination of Cs-137 in radioactive waste waters and biological samples after on-line concentration. However, on-line concentration of Cs-137 from water samples such as seawater may be difficult because these waters contain a high concentration of bivalent cations such as Mg^{2+} and Ca^{2+} which have a higher selectivity for resins (normally used in ion chromatographic columns) than cesium ions.

For on-line preconcentration of Cs-137 from seawater, the development of ion chromatographic columns, showing specific selectivity for cesium over Mg^{2+} and Ca^{2+}, is necessary. This can be

achieved on inorganic ion exchangers as described in this review. Cesium eluted from column after selective concentration can be determined by ion chromatography.

In recent years, progress has also been made in the development of methods which can be used for direct determination of very small concentrations of cesium (radioactive and/or non-radioactive). The determination of non-radioactive or total concentration of cesium in most environmental waters, typically reported to be lower than parts per billion (ppb), also require pre-concentration. Amos et al. [113] demonstrated that by cyclic voltammetry, using a $NiFe(CN)_6^{2-}$ derivatized nickel working electrode, determination of cesium at ppb levels was possible. Determination of as little as 10^{-8} M $CsNO_3$ was possible in the presence of 1.0 M $NaNO_3$ by their method.

6. Critical comments and concluding remarks

In conclusion, pre-concentration of Cs-137 from large volumes of environmental waters needs to be carried out on inorganic ion exchangers. Organic ion-exchange resins neither showed high selectivity nor specificity for cesium and therefore were unsuitable for this purpose. A clear difference in the

Table 3

Detection limit of ^{137}Cs in seawater and other environmental samples by KCFC column method (reproduced from Ref. [41])

Material analyzed	Volume	Detector limit, pC l[-1]		
		Gamma counting 2×2.5-inch NaI crystal with 0.75×1.5-inch well	Gamma spectrometry	
			3×3-inch NaI crystal	9×9-inch NaI crystal with 3×6-inch well
Milk by disposable column method	1 l	35	33	12
Milk by dual column method	1 gallon	–	9	3
Urine	1.5 l	23	22	6
Sea water	50 gallon	–	0.2	0.07
Fresh water	1 gallon	10	9	3

selectivity of cesium on inorganic and organic ion exchangers is listed in Table 1.

Ion-exchange determination of Cs-137 in environmental waters most frequently employed AMP. This exchanger showed very high selectivity for cesium which remained almost unaffected by the presence of other ions normally found in seawater. The only problem with this ion exchanger was its microcrystalline form which resulted in low flow-rates.

This problem of low flow-rates inspired Boni [41] to employ KCFC for the determination of Cs-137 in a variety of environmental and biological samples. KCFC can be prepared in the form of hard granules, suitable for column use. Different combinations of a dual column containing organic resins in the top layer and KCFC in the bottom layer as listed in Table 2 were used to eliminate the interference by other radionuclides in gamma-ray spectrometric determination of Cs-137. In addition to seawater, determination of Cs-137 was also carried out in other environmental and biological samples as listed in Table 3. The drawback of this method, as cited by other workers, was the irreversible adsorption of cesium. The irreversibility of cesium adsorption on

KCFC made it impossible to reduce the volume of the sample for radioactive counting in order to raise the counting efficiency. Moreover, a large amount of exchanger had to be thrown away after only one use.

The shortcomings of irreversible adsorption of Cs-137 on KCFC and microcrystalline form of AMP inspired researchers to develop ion exchangers suitable for the selective adsorption and elution of Cs-137 by column chromatography. Many ion exchangers were developed by the combination of

Table 5

Adsorption of ^{137}Cs on copper ferrocyanide-Amberlite IRA-904 from seawater by batch experiment (0.5 g resin) (reproduced from Ref. [96])

Volume (ml)	Percent adsorption of Cs-137 at different agitation times				
	0.5 h	1 h	3 h	6.5 h	24 h
5	99.2 (~0)*	99.8			(~0)*
50	93.1	95.0	97.1	99.1	99.9
100	59.7	82.7	92.3	98.5	99.9
500	46.7	62.4	84.8	89.3	99.1
1000	32.2	42.6	68.7	78.8	98.3

(In brackets)*: [137]Cs in Amberlite IRA-904 Cl⁻ form.

Table 4

Cs-137 concentration in surface water of the Japan Sea (August, 1967) (reproduced from Ref. [87])

St. No.	Lat. N	Long. E	Cs-137, pC l[-1]		
			a	b	c
5	38°06'	134°27'	0.26±0.01	0.23±0.01	0.24±0.04
12	41°02'	132°15'	0.22±0.01	0.22±0.01	0.21±0.04
15	40°14'	135°12'	0.22±0.01	0.20±0.01	
18	39°31'	138°11'	0.23±0.01	0.23±0.01	

a=Data obtained with AMP–SiO₂ method; b=data obtained with KCFC–SiO₂ method; c=data obtained by Miyake et al. [99].

Table 6
Uptake of ^{137}Cs on copper ferrocyanide-Amberlite IRA-904 from seawater by column method (1.0 cm diameter, 3.0 g resin) (reproduced from Ref. [96])

Volume of seawater (ml)	Flow-rate (ml/min)	Adsorbed (%)
1500	2	99.9
1500	8	99.9
1500	15	99.8
3000	15	99.4
1500	18	94.4
3000	18	90.9

inorganic ion exchangers and inorganic and organic support for this purpose. For example, Terada et al. [87] investigated the preparation of AMP, KCFC and NCFC supported on silica gel for their application in the determination of Cs-137 in environmental waters. These exchangers were applied for the determination of Cs-137 concentration of surface waters from the Japan Sea. Near-quantitative adsorption of Cs-137 was obtained from 100 l of seawater on a wider column containing 10 g exchanger at a flow-rate of 10 l h^{-1}. An excellent agreement between AMP–SiO$_2$, KCFC–SiO$_2$ and co-precipitation methods [99] (Table 4) shows good accuracy of Cs-137 determination.

Although both methods, i.e., preconcentration (of Cs-137) by batch adsorption and column chromatography, generated quantitative results, the latter was found to be faster than the batch adsorption method as had been demonstrated by Watari and co-workers [96,97] (Table 5 and Table 6). These authors also demonstrated that preconcentration of cesium on copper(II) hexacyanoferrate(II) precipitated onto an anion-exchange resin (CuFoC/anion exchanger) was caused by the CuFoC and not by the organic resin (Table 5).

Inorganic ion exchangers precipitated on anion-exchange resins and SiO$_2$ matrices showed good column properties, yet their structural characterization has not been reported. In my view a better characterization of these resins will be helpful in the development of inorganic/organic resins with fast elution of cesium which may be used for the on-line concentration of cesium for its determination by ion chromatography.

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