

Stability of Prussian blue bound to anion-exchange resin beads for radiocaesium reduction in foodstuffs

G. B. Bengtsson* & O. I. Skorbakk†

MATFORSK, Norwegian Food Research Institute, Osloveien 1, N-1430 Ås, Norway

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Emergency decontamination of foodstuffs may be necessary after an extensive radioactive fallout causing food shortages. Prussian blue bound to spherical inert beads would be suitable for radiocaesium reduction if leaching of Prussian blue components could be minimized. Prussian blue was synthesized by consecutive binding of its constituents to macroreticular anion-exchange resin beads. After various incomplete synthesis cycles (i.e. $[\text{Fe}(\text{CN})_6]^{4-}$ binding last), the beads (designated RCF_{1.5}, RCF_{2.5}, RCF_{3.5}) leached significantly larger amounts of soluble iron than beads of complete synthesis cycles (Fe^{3+} binding last; beads designated RCF₁, RCF₂, RCF₃, RCF₄). Most of the release from RCF_{1.5}–RCF_{3.5} beads could be accounted for as $[\text{Fe}(\text{CN})_6]^{3-}$, whereas RCF₁–RCF₄ beads did not leach this substance. Repeated rinsing of RCF₃ beads reduced the leach to a minimum. The same extent of leach reduction was also accomplished by treatment with KH_2PO_4 , water-glass, a meat extract or an artificial meat fluid. Treatment with $\text{P}_2\text{O}_7^{4-}$ or $\text{P}_3\text{O}_{10}^{5-}$ destabilized the RCF₃ beads. Properly prepared composite beads after complete cycles of Prussian blue synthesis may be usable for safe reduction of radiocaesium in foodstuffs, at least in meat. © 1997 Elsevier Science Ltd. All rights reserved

INTRODUCTION

Prussian blue, a group of iron(III) hexacyanoferrates(II), and some other metal hexacyanoferrates(II), have been known for decades to be very selective binders of caesium ions (Cs^+). This property has been utilized in procedures for treatment of radioactive waste (Jakobi & Streat, 1991), in antidotal therapy for radiocaesium in humans (e.g. Lipsztein *et al.*, 1991), for reduction of radiocaesium absorption in domestic animals (e.g. Hove & Hansen, 1993), and for decontamination of radioactive foodstuffs (Nielsen *et al.*, 1987; Watari *et al.*, 1988; Allgäuer Alpenmilch, 1989; Gahlmann *et al.*, 1989; Bengtsson, 1989; Giese *et al.*, 1989; Bortun *et al.*, 1993).

For the treatment of foodstuffs, especially in column procedures, a bead form of the adsorbent is useful. However, satisfactory beads of solid hexacyanoferrates(II) are not easily prepared (Jakobi & Streat, 1991). Therefore, hexacyanoferrates(II) bound to spherical ion-exchange beads of organic polymers (Watari *et al.*, 1988; Gahlmann *et al.*, 1989; Bengtsson, 1989; Giese *et al.*, 1989) or

bound to granules of titanium phosphate (Bortun *et al.*, 1993) have been used for radiocaesium reduction in fluid foodstuffs. These preparations are made by consecutive treatment of the carrier with solutions of the constituents of the metal hexacyanoferrate(II) (i.e. $[\text{Fe}(\text{CN})_6]^{4-}$) and a soluble salt of a polyvalent metal.

In all applications, it is important that the adsorbent preparations have sufficiently high chemical stabilities. Numerous studies on animals and humans have shown that orally administered Prussian blue has a very low toxicity in spite of a partial breakdown in the gastrointestinal tract (for reviews see Pearce, 1994; Bengtsson, 1995). Virtually all of the released free iron, hexacyanoferrate and cyanide is metabolized and excreted by the organism (Nielsen *et al.*, 1990a,b). The stability of hexacyanoferrate(II) in relation to decontamination of foodstuffs has, however, been investigated only to a very small extent (Gahlmann *et al.*, 1989; Bengtsson, 1989; Bortun *et al.*, 1993). Prussian blue bound to polystyrene–divinylbenzene beads via quaternary ammonium groups (Amberlite IRA-904) or via iminodiacetate groups (Chelex 100) had very different chemical stabilities (Bengtsson, 1989). This could have been due to the different final steps of Prussian blue synthesis onto the carrier beads (i.e. treatment with Fe^{3+} for the

*To whom correspondence should be addressed.

†Present address: A/S FORMA, Postboks 6779, St Olav's Plass, N-0130 Oslo, Norway.

Amberlite beads, and with $[\text{Fe}(\text{CN})_6]^{4-}$ for the Chelex beads) and not primarily due to the carrier properties *per se*. In a study of copper hexacyanoferrate(II) immobilized on titanium phosphate, an acceptable stability was only observed in solutions of very high ionic strength (Bortun *et al.*, 1993).

In the present study, we have investigated the chemical stability of Prussian blue bound to Amberlite IRA-904 beads after complete cycles (Fe^{3+} binding last) and incomplete cycles ($[\text{Fe}(\text{CN})_6]^{4-}$ binding last) of Prussian blue synthesis, together with possible ways to minimize the leaching of Prussian blue components, with emphasis on the application in meat processing. A short version of the results was recently presented at an international symposium (Bengtsson & Skorbakk, 1995).

MATERIALS AND METHODS

Chemicals

Reagents were of p.a. grade and obtained from various sources. The water was deionized and distilled.

Washing of anion-exchange beads

Amberlite IRA-904 beads, 16–50 wet mesh, Cl^- form, were from Rohm and Haas (Philadelphia, PA, USA). Two hundred grams (about 84 g dry mass) of beads in a beaker were rinsed in ten 600 ml changes of water, while decanting off the very fine particles. The following treatments were carried out during stirring with a suspended Teflon paddle (15 mm \times 15 mm, 1000 rpm) and completed by aspiration of the fluid from the bottom by means of a tube covered in nylon mesh (Mann & Casso, 1984) and a peristaltic pump. The wet beads were treated with 1 bed-volume (320 ml) of 5 M HCl for 5 min, rinsed with 600 ml of water, treated for 5 min with 1 bed-volume of 5 M NaOH and rinsed with 600 ml of water. This treatment cycle was repeated once, followed by two extra rinses in water. This procedure eliminated any unpleasant smell from the beads.

Binding of Prussian blue to polymer beads

The preparation of the composite beads was based on the method of Mann and Casso (1984) and earlier procedures by Watari and Izawa (1965), Watari *et al.* (1967, 1968), Bonnin and Poirier (1969) and Folsom *et al.* (1975), using the stirring and aspiration techniques described above. A complete cycle of Prussian blue synthesis was carried out at 20–23°C as follows, each treatment/rinse being of 10 min duration. About 84 g dry mass of washed Amberlite IRA-904 beads after removal of the last rinse-water (see above) was treated with 250 ml of 0.5 M $\text{K}_4\text{Fe}(\text{CN})_6$, rinsed three times with 500 ml of water and treated with 250 ml of 1 M FeCl_3 , followed by three water rinses. Products after 1–4 complete cycles,

denoted RCF₁, RCF₂, RCF₃ and RCF₄, and products after incomplete cycles (before treatments 2, 3 and 4 with FeCl_3), denoted RCF_{1.5}, RCF_{2.5} and RCF_{3.5}, were dried and stored at room temperature.

Additional rinsing

Dry RCF₃ beads were rinsed (10 min, 5 g + 60 ml) by stirring as during preparation, 6 or 12 times in water, with or without three initial rinses in 0.1 M HCl.

Special chemical treatment

Dry RCF₃ beads were treated as above (10 min, 5 g + 60 ml) with 60 mM KH_2PO_4 (pH 4.6), 60 mM $\text{K}_4\text{P}_2\text{O}_7$ (pH 5.9, adjusted with CH_3COOH), 0.39 M $\text{Na}_5\text{P}_3\text{O}_{10}$ (pH 8.1), 0.39 M $\text{Na}_5\text{P}_3\text{O}_{10}$ (pH 6.7, adjusted with CH_3COOH), 3.7 g litre⁻¹ $\text{Na}_2(\text{SiO}_2)_{3.6}$ (pH 4.7, adjusted with CH_3COOH), an artificial meat fluid or a meat extract. Beads treated with 0.9% NaCl were used as a control. After removal of the fluids, the beads were rinsed three times in water as above and dried at room temperature.

Artificial meat fluid

The composition was based on inductively coupled plasma spectrometric (ICP) analysis of the aqueous phase of a reindeer meat homogenate after ultra-centrifugation: ≈ 110 mM K^+ , 25 mM Na^+ , 8.5 mM Mg^{2+} , 0.5 mM Ca^{2+} , 60 mM H_2PO_4^- , 16 mM SO_4^{2-} , 11 mM Cl^- and 50 mM lactate. One litre is prepared by mixing 850 ml of water consecutively with 40 ml of 1.5 M KH_2PO_4 , 10 ml of 5 M lactic acid, 7.5 ml of 1 M Na_2SO_4 , 2.0 ml of 5 M NaCl, 8.5 ml of 1 M MgSO_4 , 0.5 ml of 1 M CaCl_2 , about 50 ml of 1 M KOH to pH 5.5, and finally water for volume adjustment.

Meat extract

Preparation was by gentle shaking for 18 h at +4°C of 500 g of reindeer meat (1 cm \times 1 cm pieces) in 500 g of artificial meat fluid.

Leach test

Dry Prussian blue-polymer beads (200 mg) were treated for 23 h at 20–23°C with 10 ml of 0.9% NaCl in 50 ml glass bottles on a shaking table (1 Hz, 5 cm amplitude). The wet beads were treated alike six times more with fresh saline, and the recovered fluids were analysed for light-absorbing solutes.

Analytical

Light-absorbance spectra 200–800 nm were recorded with a Hewlett Packard 8452 A diode array spectrophotometer. Soluble iron was assayed by simultaneous

ICP using a Thermo Jarrell Ash 1300 with a quantification limit of 0.06 ppm (10σ). Dry mass was determined after drying for 24 h at 105°C.

RESULTS

Release of light-absorbing material

For beads of complete cycles of Prussian blue synthesis (RCF_1 , RCF_2 , RCF_3 , RCF_4), the leach test fluids were clear and colourless with a significant light-absorbance below 400 nm only, including one peak with a variable maximum between 200 and 250 nm (Fig. 1(A)). On the other hand, the beads after various incomplete synthesis

cycles ($\text{RCF}_{1.5}$, $\text{RCF}_{2.5}$, $\text{RCF}_{3.5}$) gave yellow leach test fluids which had maximum light absorbance between 200 and 250 nm and distinct absorbance peaks at 262, 302 and 420 nm (Fig. 1(B)).

The amount of released material decreased with the number of incubations in the leach test (Fig. 1). The magnitude of release was fairly similar in beads after various complete and incomplete Prussian blue synthesis cycles, respectively. The largest variation was in the first leach test incubation for beads of complete synthesis cycles (Fig. 2).

The light-absorbance spectra of the leach test fluids from $\text{RCF}_{1.5}$, $\text{RCF}_{2.5}$ and $\text{RCF}_{3.5}$ were very similar to the spectrum of 1 mM $\text{K}_3\text{Fe}(\text{CN})_6$, which had the same three characteristic peaks at 262, 302 and 420 nm (not

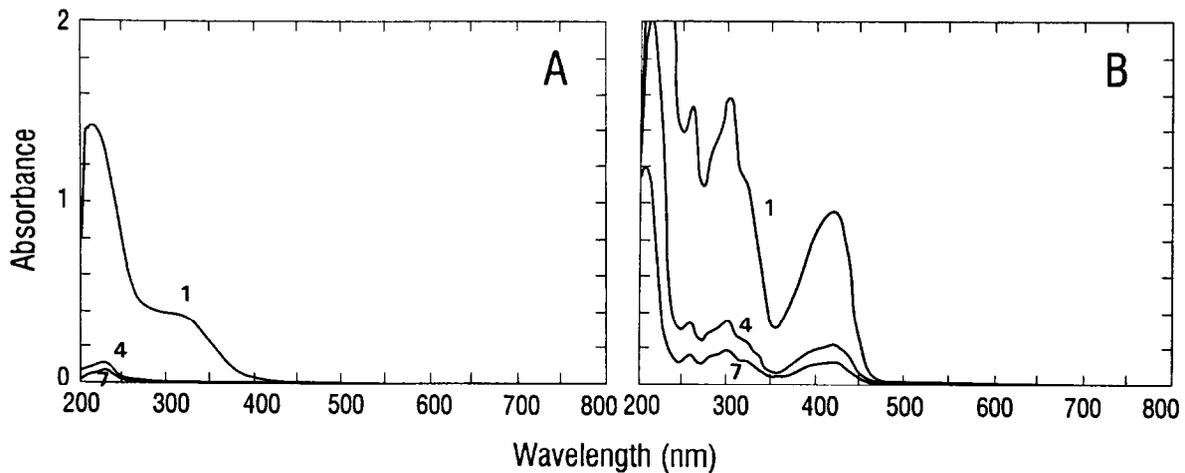


Fig. 1. Light-absorbance spectra of leach test fluids 1, 4 and 7 of Prussian blue-polymer beads after 3 (a), and 3.5 (b) cycles of Prussian blue synthesis.

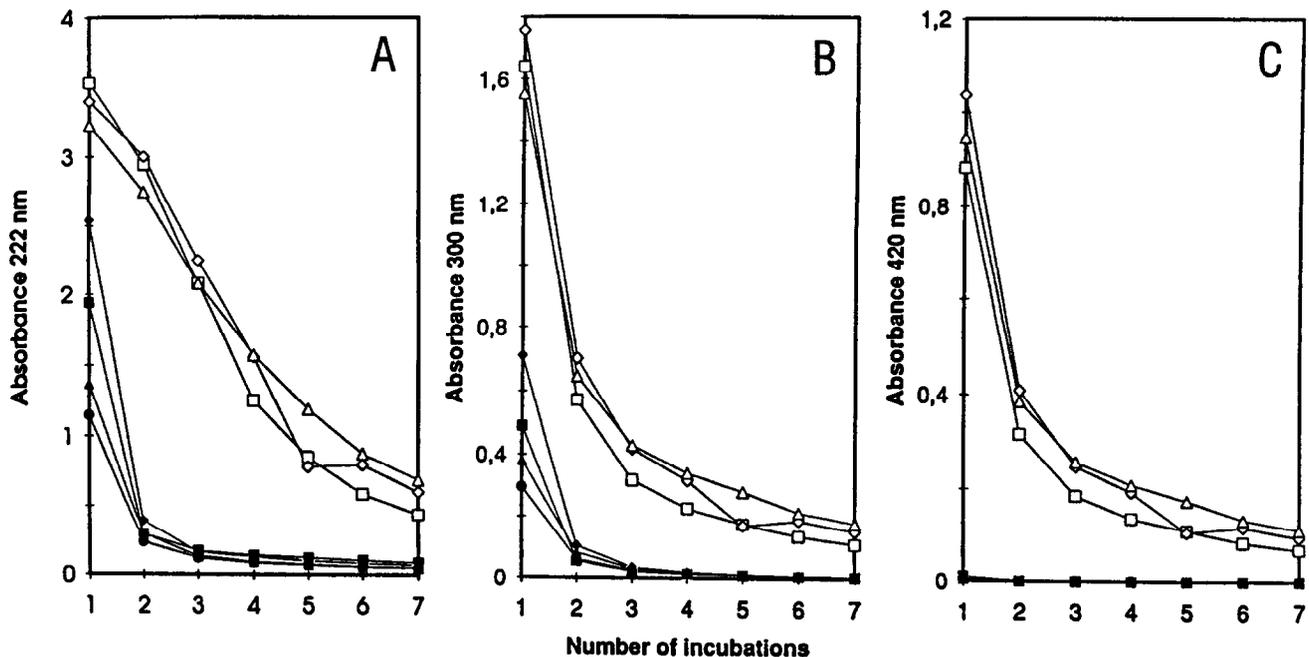


Fig. 2. Light absorbance of leach test supernatants after 1–4 complete cycles (filled symbols), and 1.5, 2.5 and 3.5 cycles (open symbols) of Prussian blue synthesis onto anion-exchange polymer beads.

shown). However, the absorbance connected with bead leach was relatively higher at lower wavelengths. For instance, in the seventh leach test fluid of RCF_{3,5} the absorbance ratios A_{222}/A_{420} , A_{260}/A_{420} and A_{302}/A_{420} were 6.2, 1.4 and 1.6 whereas, for K₃Fe(CN)₆, the ratios were 2.8, 1.2 and 1.6, respectively. The data indicate the presence of [Fe(CN)₆]³⁻ together with other light-absorbing solutes. For the beads RCF₁, RCF₂, RCF₃ and RCF₄ there was only a crude resemblance of the spectra of the first leach test fluid with the spectrum of 0.5 mM FeCl₃ (not shown).

Release of iron

Total iron analysis by ICP showed that roughly one order of magnitude less iron was released from beads RCF₁, RCF₂, RCF₃ and RCF₄ than from beads RCF_{1,5}, RCF_{2,5} and RCF_{3,5} in the leach test (Table 1). Iron concentrations calculated as [Fe(CN)₆]³⁻ (from light absorbance at 420 nm) in beads RCF_{1,5}–RCF_{3,5} or as Fe³⁺ (from light absorbance at 300 nm) in beads RCF₁–RCF₄ were lower than the ICP values, except in the seventh leach test fluid for beads RCF_{1,5}–RCF_{3,5}, where they were alike (Table 1).

Fluid pH in leach test

For beads RCF_{1,5}, RCF_{2,5} and RCF_{3,5} there was a decrease from pH 6.6 (range 6.5–6.8) in the first leach test fluid to pH 6.0 (range 5.9–6.2) in the last, whereas there was an increase for the beads RCF₁, RCF₂, RCF₃ and RCF₄ from pH 2.7 (range 2.7–2.8) to 3.7 (range 3.7–3.8). The solvent 0.9% NaCl had a pH of 4.3.

Effect of rinsing

Repeated rinsing of RCF₃ beads showed that nine rinses or more, either with distilled water alone or with combinations of dilute HCl and distilled water, reduced the leaching rate to the same extent (Fig. 3). Irrespective of postsynthesis rinsing, the leaching rate approached the same level in the last two leach test fluids.

Effect of special postsynthesis treatment

Treatment of RCF₃ beads with KH₂PO₄, a meat extract, an artificial meat fluid or dilute water-glass reduced the leaching rate considerably in comparison with repeated rinsing, whereas treatment with K₄P₂O₇ or Na₅P₃O₁₀ caused high leaching rates throughout the leach test (Fig. 4).

DISCUSSION

Whether the beads after incomplete cycles of Prussian blue synthesis released free hexacyanoferrate(III), [Fe(CN)₆]³⁻ as such or as [Fe(CN)₆]⁴⁻, followed by oxidation in the incubation fluid, is not known. Most or all of the iron released from these beads could be accounted for as [Fe(CN)₆]³⁻. The rest of the iron could have been [Fe(CN)₆]⁴⁻ or other species of soluble iron with light absorbance in the UV region. Of course, such a high level of hexacyanoferrate leach is not acceptable for a binding material to be used in foodstuff processing. However, beads prepared with complete cycles of Prussian blue synthesis (treatment with Fe³⁺ finally) released considerably lower amounts of soluble iron, devoid of detectable [Fe(CN)₆]³⁻. The leach from these beads could be reduced considerably by rinsing or by other postsynthesis treatment. It does not seem to be a stability difference between beads of different numbers of synthesis cycles. This is true both for complete and incomplete synthesis cycles. The leaching rate from Prussian blue bound to Chelex 100 decreased, however, with the number of synthesis cycles (Bengtsson, 1989).

Probably, the chemical form of Prussian blue in the beads after incomplete cycles of synthesis is largely that of colloiddally soluble Prussian blue, MFe [Fe(CN)₆] \cdot xH₂O (where M is a monovalent cation), whereas the chemical form after complete cycles of synthesis is that of 'insoluble' Prussian blue, Fe₄[Fe(CN)₆]₃ \cdot 15H₂O. The nature of the leach could be explained by a surplus of the final synthesis reagent being relatively loosely adsorbed to the outermost layer

Table 1. Iron content of leach test fluids 1, 4 and 7 measured by ICP or calculated from light absorbance as Fe³⁺ (300 nm, RCF₁–RCF₄) or as [Fe(CN)₆]³⁻ (420 nm, RCF_{1,5}–RCF_{3,5})

Bead type	Leach test fluid no.								
	1			4			7		
	Fe (ICP)	Fe (abs.)	% of ICP	Fe (ICP)	Fe (abs.)	% of ICP	Fe (ICP)	Fe (abs.)	% of ICP
mM	mM		mM	mM		mM	mM		
RCF ₁	0.401	0.273	68	0.0242	0.0072	30	0.0170	0.0033	19
RCF ₂	0.575	0.395	69	0.0236	0.011	47	0.0131	0.0040	31
RCF ₃	0.286	0.212	74	0.0165	0.011	67	0.0095	0.0030	32
RCF ₄	0.231	0.164	71	0.0125	0.0083	66	0.0068	0.0033	49
RCF _{1,5}	1.42	0.882	62	0.159	0.136	85	0.0693	0.070	101
RCF _{2,5}	1.29	1.04	80	0.220	0.193	88	0.0992	0.096	97
RCF _{3,5}	1.06	0.946	89	0.231	0.209	90	0.113	0.112	99

of Prussian blue, from where it is gradually lost to the aqueous fluids in contact with the beads. The solubility of some polyvalent metal hexacyanoferrates(II) is around 1–10 μM (Kourim *et al.*, 1964; Dvorák, 1970; Bellomo, 1970; Bellomo *et al.*, 1972), that of 'insoluble' Prussian blue being measured to 0.7 μM (Kourim *et al.*, 1964). The released amount of iron in the final leach test incubation (Table 1) would correspond to 1–3 μM of dissolved $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3 \cdot 15\text{H}_2\text{O}$ for the beads of complete Prussian blue synthesis cycles. However, we do not know the chemical form of iron in solution, but Fe^{3+} could dominate, being the last synthesis reagent.

The decreased leaching rate after treatment of RCF_3 beads with the meat-related fluids or water-glass may be explained by fixation in the beads of the surplus iron in the form of orthophosphate or silicate, respectively. On

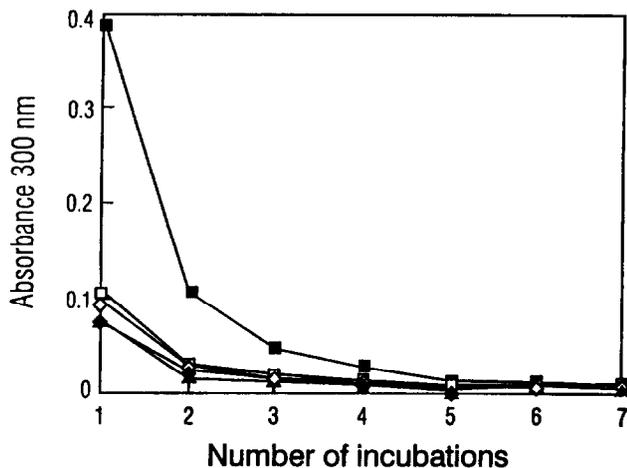


Fig. 3. Effect of postsynthesis rinsing after 3 complete cycles of Prussian blue synthesis (light-absorbance of leach test fluids). The beads were rinsed with distilled water three times (■), nine times (□) and 15 times (◆), or with 0.1 M HCl three times, followed by 9 times (◇) or 15 times (●) with distilled water.

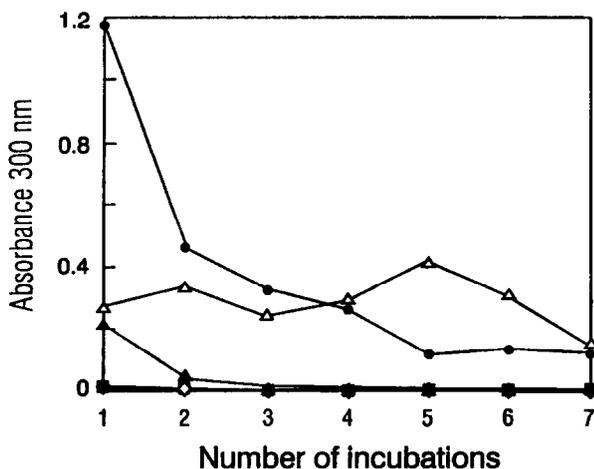


Fig. 4. Effect of postsynthesis treatment after 3 complete cycles of Prussian blue synthesis (light-absorbance of leach test fluids). The beads were treated with 60 mM KH_2PO_4 (■), artificial meat fluid (□), meat extract (◆), water-glass (◇), 0.9% NaCl (▲), 60 mM $\text{K}_4\text{P}_2\text{O}_7$ (△), or 0.39 M $\text{Na}_5\text{P}_3\text{O}_{10}$ (●).

the other hand, the polyphosphates $\text{P}_2\text{O}_7^{4-}$ and $\text{P}_3\text{O}_{10}^{5-}$ destabilized the beads. Elsewhere, it is reported that oxalate is able to convert 'insoluble' Prussian blue to the colloiddally soluble form (Remy, 1959). Thus, some chelating agents can dissolve Prussian blue, probably by lowering the concentration of free Fe^{3+} . It is of great importance for food decontamination procedures that residues of cyanide and hexacyanoferrate are controlled. In several countries some water-soluble hexacyanoferrates(II) are approved as food additives, and a joint FAO/WHO expert committee has decided the acceptable daily intake to be not more than 0.025 mg kg^{-1} body mass calculated as $\text{Na}_4\text{Fe}(\text{CN})_6$ (WHO, 1974). Reduction of radiocaesium in meat by means of the present beads after complete Prussian blue synthesis cycles, using a treatment fluid compatible with meat, would not give toxic levels of hexacyanoferrate (or free cyanide).

Gahlmann *et al.* (1989) observed a marked breakdown of the L-ascorbic acid in black current juice treated with ammonium iron(III) hexacyanoferrate(II) bound to Amberlite IRA-904 beads. Addition of synthetic ascorbic acid afterwards would, however, be a simple way to compensate for the losses, according to the authors. In the same study, the low level of free HCN was observed in several treated fruit juices. Furthermore, the level of NH_4^+ was increased due to the ammonium ion as the exchangeable ion and due to impurities of NH_4Cl in the adsorbent. We do not know the details of the production of this particular adsorbent. Since potassium is the most abundant mineral in most foodstuffs, K^+ is preferred as the exchangeable ion.

From the present study, it is concluded that properly prepared composite adsorbent beads, using a specially washed anion-exchange polymer and prepared by complete cycles of Prussian blue synthesis, followed by proper postsynthesis treatment, may be suitable for the decontamination of radioactive foodstuffs, or at least of meat. It is recommended that the stability of the adsorbent and possible negative effects should be tested for each type of foodstuff of interest.

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