

EXCHANGE CAPACITY OF AMMONIUM PHOSPHOMOLYBDATE FOR CAESIUM BY BATCH TECHNIQUE*

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INTRODUCTION

EFFORTS have increased within the past few years to search for collecting agents for the low concentration levels of radio-caesium from sea-water. Several reagents used for the precipitation of potassium have been used for concentrating caesium. Among them are the well-known sodium cobaltinitrite^{1,2}, ammonium phosphomolybdate⁴⁻⁶, and tetraphenyl boron^{7,8}. The ferrocyanides of cobalt, copper, zinconium, iron, nickel⁹⁻¹² and cobalticyanides of cobalt¹³, zinc and cadmium¹⁴ are also effective scavengers for caesium. It will be useful to have a collecting agent which will have less contamination capacity for K⁺ for a direct determination of radiocaesium by gamma spectrometry. Ammonium phosphomolybdate (AMP) in acid solutions (pH ~ 1) carries caesium quantitatively and collects only very small quantities of potassium. The aim of the present investigation is to study the carrying capacity of preformed microcrystalline ammonium phosphomolybdate in single step for caesium at various stable caesium carrier levels and the effect of chemically very similar NH₄⁺ ion on caesium recovery.

EXPERIMENTAL

Sets of three 1 litre sea-water samples were acidified to pH 1 with 20 ml of conc. HNO₃ and spiked with known amount of Cs-137 activity [16,000 dpm]. In order to find the minimum amount of AMP needed to carry caesium quantitatively, varying amounts [25-400 mg/l] of preformed microcrystalline AMP [BDH. L.R.] were added to these one litre sea-water samples, stirred and allowed to settle overnight. The precipitate was filtered through millipore filter-paper (0.22 μ size) and the filter-paper was transferred into the counting vial. The precipitates were dissolved in minimum quantities of ammonia, the heights were adjusted to the same as that of the standard and counted in 3" \times 3" well type NaI (Tl) crystal coupled to a 512 channel

Nuclear Data Analyser. The results are shown in Table I. AMP amount needed per litre

TABLE I

Optimum amount of AMP to carry Cs-137 from 1 litre sea-water

No.	Amount of AMP added mg	Cs-137 recovered %	Standard deviation %
1	25	66.7	2.4
2	50	77.7	6.4
3	100	96.0	4.2
4	200	96.6	4.1
5	400	95.7	2.3

of sea-water was fixed from these experiments and tests were carried out with 50 litres of sea-water and 200 mg AMP/litre. Results are given in Table II.

TABLE II

Recovery of Cs-137 from 50 litres sea-water

No.	Cs-137 activity (cpm)		Recovery %
	Added	Recovered	
1	4129	4025	97.5
2	4129	4032	97.7

TABLE III

Effect of NH₄⁺ ion on the recovery of Cs-137 from 1 litre sea-water

No.	Conc. of NH ₄ ⁺ g/l	Cs-137 recovered %	Standard deviation %
1	0.17	99.2	1.0
2	0.33	98.0	1.4
3	1.00	79.4	2.4
4	2.00	56.0	3.6
5	3.00	46.1	2.5
6	5.00	31.0	2.6

The effect of ammonium ion on the recovery of Cs-137 from sea-water was examined (Table III). 1 litre of filtered sea-water samples were acidified to pH 1 with 20 ml of conc. HNO₃ and spiked with known amount of Cs-137 activity. Varying amounts of ammonium chloride were added and the carrying

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capacity for Cs-137 on 200 mg AMP was studied.

TABLE IV
Effect of caesium carrier on Cs-137 recovery from 1 litre sea-water

No.	Cs carrier added mg	Cs-137 recovery %	Standard deviation %
1	Nil	96.6	4.1
2	0.02	95.5	3.9
3	0.05	99.8	1.0
4	0.10	99.0	1.0
5	0.20	95.8	2.7
6	0.50	99.8	1.0
7	5.0	99.7	1.0
8	10.0	100.0	1.0
9	20.0	76.0	3.6
10	30.0	54.5	1.2
11	40.0	42.1	1.9
12	61.0	30.0	1.0

In order to study the amount of natural caesium that can be picked up per unit weight of AMP, experiments were conducted with varying concentrations of natural caesium (along with Cs-137) in one litre of acidified sea-water samples. 200 mg AMP was used to carry caesium. Results are shown in Table IV.

DISCUSSION

It is seen from Table I that AMP quantities greater than 100 mg are sufficient to carry Cs-137 quantitatively from 1 litre of sea-water. Rocco and Broecker⁵ have concluded from their preliminary studies that 250 mg AMP per litre is sufficient to carry 90% of Cs-137 added. Further they state that it is not necessary to employ six times larger amounts of AMP per litre used by Miyake *et al.*¹⁵. For their field investigations, Rocco and Broecker have used 160 mg AMP/litre and caesium recovery averages to 55% even after the large number of steps used. Folsom¹² and co-workers have used 400 mg AMP per litre and they recommend that this quantity is needed for quantitative recovery of Cs-137 from sea-water. However, the present results indicate that no loss of caesium occurs even at AMP levels as low as 100 mg per litre. In the absence of practical problems, the safer limit of 200 mg AMP per litre can be employed even for large volumes of sea-water. The removal efficiency is confirmed by the results shown in Table II. The level of 200 mg AMP per litre yields $98.3 \pm 2.3\%$ for the recovery of Cs-137 in presence of natural caesium, which corresponds to a K_d value of $> 10^5$

compared to the value of 5×10^4 reported by Folsom and Sree Kumaran¹².

Dr. Bowen in a personal communication states "when Cs-137 was collected on AMP after ferric hydroxide precipitation (with ammonia), the mean Cs-137 found was not changed but the variance about the mean (batches of eight replicate samples) was about 3 times higher than when collected on AMP before the hydroxide precipitation". It is seen from Table III that ammonium ion concentrations upto 0.33 g/litre do not have recognizable inhibiting effect on the recovery of Cs-137. Increased amounts of ammonium ion compete with caesium exchange on AMP. Yamagata and Yamagata¹⁶ have also studied this effect in 100 ml of artificially prepared salt solutions to simulate the composition of food, urine or biological tissues. Their conclusions based on *in situ* precipitations of AMP are quite similar with ours. The fact that the quantities of ammonium ion less than or equal to 1 g NH_4^+ per litre do not inhibit Cs-137 recovery in their studies, is mainly due to six times larger amounts of AMP and *in situ* precipitation employed by them. It is interesting to note that in 0.1 M NH_4^+ concentration, the K_d value of 6,000 obtained by Smit¹⁷ using column technique agrees well with the K_d value of 7,000 obtained in the present work at the same concentration.

The carrier caesium upto 10 mg does not affect the recovery of Cs-137 from 1 litre sea-water (Table IV). Hence, from tracer concentrations upto 10 mg of caesium can be quantitatively removed on AMP from acid solutions. The maximum amount of caesium that is held on 200 mg AMP is about 18 mg, thus the ion exchange capacity of AMP by these batch studies works out to be 0.7 meq Cs/g, (Cf Table IV) which is about 45% of the exchangeable NH_4^+ (1.57 meq/g)¹⁸.

The major conclusions of the present work are:

- (1) 100 mg AMP is sufficient to carry Cs-137 quantitatively from 1 litre of sea-water.
- (2) With 200 mg AMP, 10 mg caesium can be quantitatively carried from 1 litre of sea-water, and
- (3) NH_4^+ concentrations higher than 0.33 g/l interfere with the carrying of Cs-137 when 200 mg AMP is used per litre of sea-water.

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OBSERVATIONS ON THE CYTOLOGY OF THE MADRAS MINT

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THE term mint, often applied to various species of *Labiatae*, is most frequently used to designate plants of the genus *Mentha* in which are included about 30 species of perennial herbs which are natives of the North Temperate Zone. Mints hybridize freely in nature, giving rise to integrating forms which make the limitations of certain species difficult. They have been in cultivation from ancient times for their aromatic oils which are used in culinary preparations, in medicine and perfumery.

Cytologically the genus *Mentha* falls into two well-defined groups. The *Pennyroyal* or *Pulegium* group with a basic number $x=10$ which is confined to the Mediterranean region and the "*Spicata-Arvensis*" group with basic number $x=6$ or $x=12$ which has a much wider distribution. The lowest chromosome number of this group is found in *M. longifolia* which has 24 chromosomes. Polyploidy is common in this group with chromosome numbers $2n=48$ and 72 in *M. piperata* and $2n=96$ in *M. arvensis*, *M. citrata* and *M. aquatica* (Sobti,

1965). *M. arvensis* vari *piperascens*, popularly known as the "Japanese mint", was introduced into India and is now extensively grown for the production of menthol. A colchipploid of the Japanese mint with $2n=192$ chromosomes was produced at the Regional Research Laboratory, Jammu, in 1960 (Janaki Ammal and Sobti, 1962). It is more robust but has thicker stems than the Japanese mint which is a disadvantage in commercial cultivation. To rectify this defect the Jammu mint was backcrossed with the Japanese mint. The progeny was found to be intermediate in vegetative characters (Fig. 1). Roots tip squashes of the hybrid showed $2n=144$ chromosomes (Fig. 2), and it may therefore be considered as a "triploid" form of the Japanese mint. It flowered for the first time at the Botany Field Research Station of the University of Madras in 1970 and has thus been designated as the "Madras mint".

Meiosis was studied in pollen mother cells and the 144 chromosomes were found to be associated chiefly as bivalents and univalents