

## PRODUCT SHEET

### Cs resins

#### Main applications

- Concentration and separation of Cesium

#### Packing

Order N°.	Form	Particle size
HC-B50-M, HC-B100-M, HC-B200-M	50, 100, 200g bottles AMP-PAN resin	100-600 $\mu\text{m}$
HC-C200-M <i>Available upon request</i>	200 x 2mL columns of AMP-PAN resin	100-600 $\mu\text{m}$
HC5-C20-M, HC8-C20-M, HC10-C20-M <i>Available upon request</i>	20 x 5, 8, 10mL columns of AMP-PAN resin	100-600 $\mu\text{m}$
NC-B50-M, NC-B100-M, NC-B200-M	50, 100, 200g bottles KNiFC-PAN resin	100-600 $\mu\text{m}$
NC-B50-I, NC-B100-I, NC-B200-I	50, 100, 200g bottles KNiFC-PAN resin	300-800 $\mu\text{m}$

#### Physical and chemical properties

Density : AMP-PAN: 0.27 g dry resin.mL<sup>-1</sup> ; ~1g wet resin.mL<sup>-1</sup> ;  
KNiFC-PAN: 0.20 g dry resin.mL<sup>-1</sup> ; ~1g wet resin.mL<sup>-1</sup>.

Capacity : 33 mg Cs/g dry AMP-PAN resin

#### Conditions of utilization

Recommended T of utilization : /

Flow rate : Depending on matrix flow rates up to 300 mL/min might be applied

Storage : Dry and dark, T<30°C, resin needs to be kept wet during storage

Matrices:

Matrix	Resin	Particle size
Acidified sea water	AMP-PAN	100 – 600 $\mu\text{m}$
Liquid radioactive waste	AMP-PAN	100 – 600 $\mu\text{m}$
Natural waters	KNiFC-PAN	100 – 600 $\mu\text{m}$
Urine and milk samples	KNiFC-PAN	300 – 800 $\mu\text{m}$

*For additional information see enclosed literature study*

## LITERATURE STUDY

### Cesium resins

Both resins, AMP-PAN and KNiF-PAN have been developed by Dr. Šebesta at the Czech Technical University in Prague. Like the  $\text{MnO}_2$ -PAN resin both resins are based on very fine and selective inorganic materials embedded in an organic matrix based on polyacrylonitrile (PAN) in order to improve their mechanical characteristics. The active components are the widely employed ammonium phosphomolybdate (also **Ammonium MolybdoPhosphate**, AMP) and potassium nickel hexacyanoferrate(II) (also potassium **Nickel FerroCyanate**, KNiFC).

Both resins are used for the concentration and separation of Cs from various liquid samples.

AMP-PAN resin is based on ammonium phosphomolybdate, an inorganic ion exchanger known for its high selectivity for Cs even at elevated acid concentrations, quick kinetics and radiation stability [1].

One of the main restraints to the use of AMP is its unfavorable microcrystalline structure accordingly considerable work has been performed to improve its granulometry. Embedding the AMP in an organic matrix allows for controlling particle size, topography, porosity, hydrophilicity and cross-linking of the resin matrix as well as the amount of AMP embedded in the resin.

Šebesta and Štefula showed that embedding the AMP in a PAN matrix only has limited impact on its Cs uptake kinetics, which remain very rapid, and on the Cs capacity of the embedded AMP [1]. It could further be shown that the resin is chemically stable even under relatively harsh conditions such as 1M  $\text{HNO}_3$  / 1M  $\text{NaNO}_3$  or 1M  $\text{NaOH}$  / 1M  $\text{NaNO}_3$ , even after storing the resin under these conditions for 1 month no visible mechanical damage could be observed,  $K_D$  values, sorption kinetics and capacity also remained unchanged [2]. Radiolysis stability of the resin was evaluated in acidic solution by exposing it to doses up to  $10^6$  Gy, again no changes in  $K_D$  or sorption capacity were found.

Desorption of the cesium is only possible using concentrated ammonium salts, 10 bed volumes of 5M  $\text{NH}_4\text{Cl}$  for example elute 92% of Cs from a column [1] (alternatively  $\text{NH}_4\text{NO}_3$  might be used [3]) or by destruction of the AMP using strong alkaline solutions (like 5M  $\text{NaOH}$ ).

Its high selectivity for Cs even under harsh chemical conditions and high levels of radioactivity make the AMP-PAN resin a candidate resin for the treatment of radioactive waste solutions. Brewer et al. [3] tested the resin

for the removal of Cs-137 from real and simulated acidic high-active liquid radioactive waste containing high amounts of potassium and sodium. Small scale tests were performed using 1.5 mL columns and two feed solutions, one simulated tank waste (spiked with  $100 \text{ Bq.mL}^{-1}$  Cs-137) and one actual tank waste. Both solutions were filtered, and pumped through the column using a pump system at a flow rate of 26 – 27 bed volumes per hour, aliquots were taken at regular intervals and analyzed for Cs-137 activity. After the experiment the AMP-PAN columns were eluted using 30 bed volumes of 5M  $\text{NH}_4\text{NO}_3$ , reconditioned and the effluents were passed over the column a second time. For the real waste samples a Cs breakthrough of 0.15% was observed after a sample loading volume of 1000 bed volumes during the first loading cycle (corresponding to a Cs decontamination factor greater than 3000) and 0.53% after 830 bed volumes during the 2<sup>nd</sup> loading cycle. Cs recoveries in the respective eluates were 87%.

AMP-PANs robustness against high salt concentrations also makes it interesting for use in environmental analysis, especially the analysis of Cs-134/7 in sea water.

Pike et al. [4] used AMP-PAN for concentrating and purifying Cs from 20L seawater samples (acidified to pH 1 – 2, stable Cs was added for yield determination by ICP-MS). The authors employed 5 mL columns and worked at a flow rate of  $35 \text{ mL.min}^{-1}$ . After extraction the resin was rinsed from the column using 0.1M  $\text{HNO}_3$  and analysed by gamma spectrometry. Yields were found to be  $93.5\% \pm 5.0\%$  ( $n=55$ ). The authors further analysed an internal lab standard (WHOI) in triplicate and IAEA sea water reference material, results are summarized in table 1.

*Table 1: Comparison obtained and reference values, sea water samples [4]*

Sample reference	Reference value / $\text{Bq.m}^{-3}$	Obtained value / $\text{Bq.m}^{-3}$
WHOI	$3.4 \pm 0.4$	$3,7 \pm 0.2$
IAEA-443	340 - 370	$369 \pm 8$

Even larger seawater samples were analysed by Kamenik et al. [5]. The authors evaluated, in addition to the AMP-PAN resin, also the use of KNiFC-PAN resin, which is based on potassium-nickel hexacyanoferrate(II) embedded in a PAN matrix.

The authors passed 100L of acidified seawater samples (in case of KNiFC-PAN unacidified seawater samples were tested as well) through 25

## LITERATURE STUDY

mL beds of AMP-PAN or KNiFC-PAN resin at flow rates up to  $300 \text{ mL} \cdot \text{min}^{-1}$  allowing for processing 100L samples in less than 6h. As described before stable Cs was added to the seawater samples to allow for the determination of the chemical yield e.g. via ICP-MS. After loading resins were rinsed from the columns, dried and measured by gamma spectrometry using a coaxial HPGe detector with 43% rel. efficiency in Petri dish geometry. Chemical yields obtained are summarized in table 2. Yields are generally high, KNiFC-PAN showing slightly higher yields for the acidified seawater samples than AMP-PAN resin and comparable chemical yields for acidified and non-acidified seawater samples.

**Table2:** Comparison of obtained chemical yields, 100 L sea water samples, AMP-PAN and KNiFC-PAN [5]

Resin	Matrix	Chemical yield / %
AMP-PAN	sea water (pH 1)	88,1 +/- 3,3
KNiFC-PAN	sea water (pH 1)	92,9 +/- 1,1
KNiFC-PAN	sea water	90,2 +/- 2,7

Higher flow rates were tested for the processing of non-acidified sea water samples on KNiFC-PAN resin; even at a flow rate of  $470 \text{ mL} \cdot \text{min}^{-1}$  Cs yield is still greater than 85%.

The authors calculated the minimum detectable activity (MDA) for 100L samples at 50 – 70 h counting time and average chemical yields. For Cs-137 they calculated an MDA of  $0.15 \text{ Bq} \cdot \text{m}^{-3}$  and  $0.18 \text{ Bq} \cdot \text{m}^{-3}$  for Cs-134.

KNiFC-PAN resin was further used for the determination of Cs isotopes in milk [6] and urine [7].

Other than for Cs separation AMP based ion exchangers have also been used to separate Rb from other alkalines in acidic media [8, 9].

## Bibliography

- (1) Sebesta F, Stefula V (1990) Composite ion exchanger with ammonium molybdophosphate and its properties. J Radioanal Nucl Chem 140(1):15 - 21
- (2) John et al. (1999) Application of new inorganic-organic composite absorbers with polyacrylonitril binding matrix for separation of radionuclides from liquid radioactive wastes. Choppin and Khankhasayev (eds.) Chemical separation technologies and related methods of nuclear waste management, 155 - 168
- (3) Brewer et al. (1999) AMP-PAN column tests for the removal of Cs-137 from actual and simulated INEEL high-activity wastes. Czechoslov J Phys 49(S1):959-964
- (4) Pike et al.. (2012) Extraction of cesium in seawater off Japan using AMP-PAN resin and quantification via gamma spectroscopy and inductively coupled mass spectrometry. Radioanal Nucl Chem. DOI 10.1007/s10967-012-2014-5
- (5) Kamenik et al. (2012) Fast concentration of dissolved forms of cesium radioisotopes from large seawater samples. J Radioanal Nucl Chem. DOI 10.1007/s10967-012-2007-4
- (6) Kamenik J et al. (2009) Long term monitoring of Cs-137 in foodstuffs in the Czech Republic. Appl Radiat Isot 67(5):974-977
- (7) Bartuskova et al. (2007) Ingestion doses for a group with higher intake of Cs-137. In: IRPA regional congress for Central and Eastern Europe, Brasov, Romania
- (8) Coetze CJ: The separation of a sodium-rubidium mixture on an ion exchanger. (1972) J Chem Edu 49(1): 33
- (9) Smit, J van R, Robb W, Jacobs JJ: Cation exchange on ammonium molybdophosphate—I: The alkali metals (1959) J Inorg Nucl Chem, 12(1-2): 104-112