Application of Extraction Chromatography for Determination of Radionuclides (U, Th, Ra, Pb Isotopes and ²¹⁰Po) in Drinking Water Samples

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1. Introduction

• The advantage of the extraction chromatographic methods:

- (1) Better selectivity if compared with the liquid-liquid extraction method.
- (2) There is a wide variety of comercially available products served for different analytical purposes.
- (3) Beside the comercially available products, it can easily be prepared in laboratory with the extractants and the inert support.
- Prof. C. Testa is a pioneer in the application of the extraction chromatographic methods for radionuclide analyses, not only in Italy, but also in the world. His research activities can be traced back to 1960's.

1. Introduction

- The National Institute of Environmental Protection and Research (ISPRA) has successfully used the extraction chromatographic methods for separation and determination of the fission products, rare-earth elements, and trans-uranic elements, including ¹⁴⁴Ce, ⁹⁰Sr-⁹⁰Y, ²¹⁰Po, ²¹⁰Pb, ²³⁸U, ²³⁴U, ²³²Th, ²³⁰Th, ²²⁸Th, ²²⁶Ra, ²²⁸Ra, ²³⁹⁺²⁴⁰Pu, ²⁴¹Am in environmental and biological samples, for examples:
- Microthene-TNOA: For determination of Pu isotopes;
- Microthene-TOPO: For determination of U and Ra isotopes;
- Microthene-TOPO: For determination of Th isotopes;
- **Microthene-HDEHP: For determination of** ⁹⁰**Sr and** ²⁴¹**Am.**
- **The anion-exchange resin, BIO-RAD-AG 1-X4, for Ra analyses.**
- **The cation-exchange resin, AG-50W-X8, for Pb analyses.**

2. Materials

- 2.1 Inert support:
- Microthene (microporous polyethylene or polypropylene, 60 -140 mesh): which are the products of petrochemistry industry.
- There are three main advantages of using Microthene:
- (1) It is an easily available material.
- (2) Its cost is very low if compared with that of Kel-F and other similar products.
- (3) After impregnating with different organic extractants, such as TOPO, HDEHP, TNOA, TBP etc, it can easily be prepared into columns with different capacity for different analytical purposes.

2.2 Stationary phase used in Lab. of the ISPRA:

The organic extractants can be:

- TOPO (tri-octyl-phosphine oxide);
- HDEHP (di(2-ethyhexyl)phosphoric acid);
- TNOA (Tri-n-octylamine);
- TBP (tri-n-butyl phosphate), etc.
- 2.3 Mobile phase:
- Feeding solution: acid solution (HCl, HNO₃, H₂SO₄).

2.4 Column preparation

- A certain amount of TOPO or TNOA or HDEHP was dissolved or diluted in about 100 ml of cyclohexane or toluene in a beaker. A certain amount of Microthene was added. The mixture was stirred for several minutes until homogeneous, and was then evaporated to eliminate cyclohexane or toluene at 50 °C.
- The porous powder thus obtained contained about 10-20% of TOPO or TNOA or HDEHP.
- A portion of the powder, slurred with 3 ml of concentrated HCl and some water, was transferred to a chromatographic column. After conditioning, the column was ready for use.

2.5 Chromatographic column.



3 Methods

3.1 Procedure for determination of uranium isotopes in water samples by α -spectrometry.



Uranium alpha-spectra obtained from a water sample by using the recommended procedure for uranium.





3.2 Procedure for determination of thorium isotopes in water samples by alpha-spectrometry.



Thorium alpha-spectra obtained from a soil sample by using the recommended procedure for thorium.



Fig. 1. Alpha-spectra of thorium isotopes and their daughters obtained from a sample (IAEA-326 soil) by using the recommended procedure (T=5681 min).

3.3 Procedure for determination of radium isotopes in water samples by alpha-spectrometry.



Radium alpha-spectra obtained from a water sample by using the recommended procedure for radium.



Fig. 7. Alpha-spectra of radium and thier daughters obtained from a water sample by using the recommended procedure.

3.4 Procedure for determination of ²¹⁰**Po**, ²¹⁰**Pb and** ²¹²**Pb in** water samples.



Polonium alpha-spectra obtained from a water sample by using the recommended procedure for Po.



Fig. 2. Alpha-spectra of 209 Po (tracer) and 210 Po obtained from a water sample using the recommended procedure.









the ²¹²Pb contribution) of a Pb source obtained from a potable water sample (same water as shown in Fig. 1) collected in Italy.



source obtained from a tap water sample collected in Italy.





3.5 The minimum detectable activity (MDA) of the methods for the radionuclides determined (counting time: about 10 days for alphaemitters and 3 days for beta-emitters).

Radionuclide	Blank counts, cps	Counting efficiency, %	Yield, %	Sample volume, L	MDA, mBq L ⁻¹
²³⁸ U	$0.000085 {\pm} 0.000017$	30.06	75.4±9.0	1.00	0.22
²³⁴ U	$0.000085 {\pm} 0.000017$	30.06	75.4±9.0	1.00	0.22
²³⁵ U	0.0000065±0.0000046	30.06	75.4±9.0	1.00	0.061
²³² Th	0.0000091±0.0000034	31.08	74.7±14.2	100	0.00044
²³⁰ Th	0.000033±0.000006	31.08	74.7±14.2	100	0.00080
²²⁸ Th	0.000053±0.000008	31.08	74.7±14.2	100	0.0010
²²⁶ Ra	0.00014 ± 0.00002	31.77	86.2±6.5	2.00	0.11
²²⁴ Ra	0.00014 ± 0.00002	31.77	86.2±6.5	2.00	0.11
²²⁸ Ra	0.00014 ± 0.00002	31.77	86.2±6.5	2.00	0.11
²¹⁰ Po	0.000031 ± 0.000007	28.77	94.8 ± 3.8	5.00	0.016
²¹⁰ Pb(²¹⁰ Bi)	0.00607 ± 0.00027	48.16	$\textbf{88.8} \pm \textbf{5.5}$	48.0	0.039
²¹² Pb(²¹² Bi)	0.00607 ± 0.00027	88.36	$\textbf{88.8} \pm \textbf{5.5}$	48.0	0.033

4.0 Results and discussion

4.1 The ²³⁸U, ²³⁴U, ²³⁵U, ²³²Th, ²³⁰Th, ²²⁸Th activity concentrations (in mBq L⁻¹) in drinking water samples collected in Italy.

mple	Commercial name	²³⁸ U	²³⁴ U	²³⁵ U	²³⁴ U/ ²³⁸ U	²³⁵ U/ ²³⁸ U	²³² Th	²³⁰ Th	²²⁸ Th	²³⁰ Th/ ²³² Th	²²⁸ Th/ ²³² T h
1	Blues Aura	16.8±0.9	17.1±0.9	0.86±0.17	1.02	0.051	0.0011±0.0002	0.0021±0.0003	0.100±0.004	1.85	88.1
2	Egeria	59.8±2.4	84.4±3.3	3.31±0.33	1.41	0.055	0.0019±0.0004	$0.0053 {\pm} 0.0007$	0.927±0.057	2.7	479
3	Guizza	6.14±0.29	6.43±0.30	0.29±0.05	1.05	0.047	0.0010±0.0003	0.0006 ± 0.0004	0.0048 ± 0.0014	0.62	4.84
4	Panna	7.21±0.38	13.2±0.6	0.35±0.08	1.83	0.048	0.0012±0.0003	$0.0033 {\pm} 0.0006$	$0.0674 {\pm} 0.0032$	2.7	54.7
5	Rocchetta Brioblu	2.33±0.15	3.37±0.19	0.16±0.04	1.44	0.070	0.0019±0.0013	$0.0075 {\pm} 0.0023$	0.0830 ± 0.0067	3.9	43.2
6	Lete	20.5±1.2	23.3±1.3	0.98±0.21	1.14	0.048	0.0007±0.0002	0.0026 ± 0.0003	0.176±0.006	3.7	248
7	Vitasnella	78.5±4.2	71.4±3.8	4.10±0.54	0.910	0.052	0.0008±0.0002	$0.0015 {\pm} 0.0004$	0.166±0.006	1.9	203
8	San Gemini	14.2±0.7	13.4±0.7	0.42±0.11	0.947	0.030	0.0008±0.0003	0.0033±0.0007	0.0653±0.0037	3.9	77.2
9	B-Rocchetta	1.39±0.20	2.09±0.23	0.08±0.05	1.51	0.054	0.0008±0.0004	0.0008 ± 0.0007	0.0449±0.0033	1.1	58.6
10	Vera	12.0±0.8	15.3±1.0	0.99±0.21	1.28	0.083	0.0007±0.0002	≤ 0.0008	0.0068 ± 0.0008	≤1.1	9.67
11	San Benedetto	12.4±0.7	21.6±1.0	0.68±0.14	1.75	0.055	0.0014±0.0004	≤ 0.0008	0.325±0.013	≤ 0.57	232
12	Lieve	2.91±0.18	5.02±0.24	0.20±0.05	1.72	0.069	0.0013±0.0002	$0.0014 {\pm} 0.0003$	0.0307±0.0016	1.1	24.4
13	Ferrarelle	16.0±0.8	20.7±1.0	1.22 ± 0.18	1.30	0.077	0.0018±0.0003	$0.0017 {\pm} 0.0005$	1.32±0.05	0.92	717
14	Uliveto	4.13±0.23	8.29±0.37	0.27±0.05	2.01	0.065	0.0027±0.0014	0.0036 ± 0.0032	0.897±0.031	1.3	328
15	Capannelle	103±3	135±4	3.48±0.41	1.31	0.034	0.0019±0.0004	0.0023±0.0006	0.219±0.008	1.2	114
16	CSM tap water	0.206±0.064	0.249±0.066	<mda< td=""><td>1.21</td><td>ND*</td><td>0.0011±0.0003</td><td>0.0010 ± 0.0005</td><td>0.0649±0.0030</td><td>0.88</td><td>58.3</td></mda<>	1.21	ND*	0.0011±0.0003	0.0010 ± 0.0005	0.0649±0.0030	0.88	58.3
17	Magliana tap water	7.22±0.36	7.55±0.37	0.51±0.10	1.05	0.071	0.0013±0.0004	0.0012±0.0007	0.0014±0.0010	0.95	1.06
an±SD		21.4 ±29.7	26.4±36.3	1.12±1.30	1.35±0.33	0.053±0.020	0.0013±0.0006	0.0023±0.0019	0.265±0.393	1.7±1.2	161±194
ange		0.206-103	0.249-135	<mda-4.10< td=""><td>0.910-2.01</td><td>ND-0.083</td><td>0.0007- 0.0027</td><td>0.0008-0.0075</td><td>0.0014-1.32</td><td>≤ 0.57-3.9</td><td>1.06-717</td></mda-4.10<>	0.910-2.01	ND-0.083	0.0007- 0.0027	0.0008-0.0075	0.0014-1.32	≤ 0.57-3.9	1.06-717

4.2 The ²²⁶Ra, ²²⁸Ra, ²²⁴Ra, ²¹⁰Po, ²¹⁰Pb and ²¹²Pb activity concentrations (in mBq L⁻¹) in drinking water samples collected in Italy.

iple code	Commercial name (Origin)	²²⁶ Ra	²²⁸ Ra	²²⁴ Ra	²²⁸ Ra/ ²²⁶ Ra	²²⁴ Ra/ ²²⁶ Ra	²¹⁰ Po	²¹⁰ Pb	²¹² Pb	²¹² Pb/ ²¹⁰ Pb
1	Blues Aura (Umbria)	4.76±0.23	1.50±0.18	0.64±0.24	0.315	0.135	0.40±0.04	0.327±0.018	1.17±0.07	3.57
2	Egeria (Roma)	3.56±0.25	10.2±0.9	2.17±0.36	2.85	0.610	11.3±0.5	10.2±0.4	3.22±0.18	0.317
3	Guizza (Pescara)	1.19±0.10	1.23±0.24	1.12±0.23	1.03	0.941	0.50±0.04	3.62±0.15	1.12±0.08	0.308
4	Panna (Firenze)	2.49±0.17	1.95±0.27	0.35±0.16	0.782	0.141	3.39±0.20	5.11±0.21	1.77±0.11	0.346
5	Rocchetta (Perugia)	2.72±0.20	1.18±0.21	0.73±0.21	0.432	0.267	1.01±0.06	1.78±0.08	2.82±0.15	1.58
6	Lete (Caserta)	3.07±0.21	2.92±0.38	0.90±0.24	0.949	0.292	1.37±0.11	3.26±0.14	1.67±0.11	0.512
7	Vitasnella (Brescia)	26.6±1.2	5.01±0.41	0.93±0.16	0.189	0.035	7.37±0.45	8.65±0.36	3.17±0.18	0.367
8	Sangemini (Terni)	8.74±0.47	3.47±0.33	0.64±0.19	0.397	0.073	1.29±0.10	1.80 ± 0.08	3.14±0.17	1.74
9	Brioblu Rocceetta (Perugia)	1.61±0.11	0.74±0.22	0.53±0.26	0.461	0.327	5.93±0.36	1.44±0.06	2.79±0.15	1.94
10	Vera (Padova)	0.50±0.06	0.55±0.11	0.46±0.17	1.09	0.912	1.48±0.09	6.66±0.28	1.93±0.11	0.289
11	San Benedetto (Vinece)	0.52±0.06	0.10±0.14	<mda< td=""><td>0.200</td><td>ND</td><td>2.71±0.19</td><td>3.69±0.15</td><td>1.63±0.10</td><td>0.442</td></mda<>	0.200	ND	2.71±0.19	3.69±0.15	1.63±0.10	0.442
12	Lieve (Perugia)	2.95±0.20	2.54±0.27	1.11±0.28	0.862	0.378	0.32±0.03	0.806±0.036	4.03±0.20	5.01
13	Ferrarelle (Caserta)	60.8±2.3	25.7±1.9	3.17±0.45	0.422	0.052	10.7±0.6	4.27±0.18	3.26±0.18	0.764
14	Uliveto (Pisa)	14.4±0.7	6.19±0.63	1.34±0.35	0.430	0.093	0.61±0.06	0.458±0.024	2.48±0.14	5.41
15	Capannelle (Roma)	1.11±0.22	4.95±0.86	1.01±0.44	4.45	0.905	6.55±0.36	15.1±0.6	5.77±0.30	0.383
16	CSM tap water (Roma)	10.8±0.6	11.8±1.1	7.97±1.12	1.10	0.741	0.13±0.01	0.191±0.12	3.22±0.19	16.9
17	Magliana tap water (Roma)	4.97±0.28	1.53±0.25	1.53±0.61	0.308	0.308	0.15±0.01	0.562±0.028	2.27±0.13	4.05
n±SD		8.87±14.9	4.80±6.32	1.45±1.84	0.957±1.097	0.371±0.324	3.25±3.72	3.99±4.11	2.67±1.15	2.58±4.08
ge		0.50 - 60.8	0.10-25.7	<mda-7.97< td=""><td>0.189-4.45</td><td>ND - 0.941</td><td>0.13 - 11.3</td><td>0.191 - 15.1</td><td>1.12–5.77</td><td>0.289-16.9</td></mda-7.97<>	0.189-4.45	ND - 0.941	0.13 - 11.3	0.191 - 15.1	1.12–5.77	0.289-16.9

4.3 The committed effective doses $(\mu Sv yr^{-1})$ to an adult in Italy from intake of naturally occurring radionuclides in the sampled drinking waters.

Sample code	2 <mark>38</mark> U	²³⁴ U	²³⁵ U	²³² Th	²³⁰ Th	²²⁸ Th	²²⁶ Ra	²²⁸ Ra	²²⁴ Ra	²¹⁰ Po	²¹⁰ Pb	²¹² Pb	Total dose, µSv yr ⁻¹
1	0.551	0.613	0.029	0.00019	0.00032	0.00523	0.973	0.755	0.031	0.351	0.165	0.0051	3.48
2	1.96	3.02	0.113	0.00032	0.00081	0.04874	0.728	5.12	0.103	9.87	5.12	0.0141	26.2
3	0.202	0.230	0.010	0.00017	0.00009	0.00025	0.243	0.619	0.053	0.442	1.82	0.0049	3.63
4	0.237	0.472	0.012	0.00021	0.00051	0.00354	0.510	0.983	0.017	2.97	2.57	0.0077	7.79
5	0.077	0.121	0.006	0.00032	0.00115	0.00436	0.556	0.592	0.034	0.885	0.895	0.0123	3.19
6	0.673	0.834	0.034	0.00012	0.00040	0.00925	0.628	1.47	0.043	1.20	1.64	0.0073	6.55
7	2.58	2.556	0.141	0.00014	0.00023	0.00874	5.43	2.53	0.044	6.45	4.36	0.0139	24.1
8	0.466	0.480	0.015	0.00014	0.00050	0.00343	1.79	1.75	0.030	1.13	0.908	0.0138	6.59
9	0.046	0.075	0.003	0.00013	0.00013	0.00236	0.329	0.374	0.025	5.20	0.724	0.0122	6.79
10	0.393	0.547	0.034	0.00012	0.00001	0.00036	0.103	0.276	0.022	1.30	3.35	0.0084	6.03
11	0.406	0.774	0.023	0.00024	0.00006	0.01710	0.107	0.053	0.003	2.37	1.86	0.0072	5.64
12	0.096	0.180	0.007	0.00021	0.00021	0.00161	0.603	1.280	0.053	0.285	0.406	0.0177	2.93
13	0.524	0.741	0.042	0.00031	0.00026	0.06953	12.4	12.9	0.150	9.35	2.15	0.0143	38.5
14	0.136	0.296	0.009	0.00046	0.00056	0.04713	2.94	3.12	0.063	0.535	0.231	0.0109	7.44
15	3.38	4.82	0.119	0.00032	0.00035	0.01149	0.227	2.49	0.048	5.74	7.59	0.0253	24.5
16	0.007	0.009	ND	0.00019	0.00015	0.00341	2.20	5.97	0.378	0.110	0.096	0.0141	8.79
17	0.237	0.270	0.017	0.00021	0.00019	0.00007	1.02	0.771	0.073	0.130	0.283	0.0100	2.81
Mean±SD	0.704±0.976	0.944±1.30	0.036±0.044	0.00022±0.00009	0.00035±0.00029	0.0139±0.0206	1.81±3.05	2.42±3.18	0.069±0.087	2.84±3.26	2.13±2.08	0.0121±0.0049	10.87±10.55
Range	0.007-3.38	0.009-4.82	ND-0.141	0.00012-0.00046	0.00001-0.00115	0.0001-0.0695	0.103-12.4	0.053-12.9	0.003-0.378	0.110-9.87	0.096-7.59	0.0049-0.0253	2.81-38.5

The mean activity concentrations (mBq L⁻¹) of the radionuclides in the analysed drinking water samples were almost in the order:

4.4 The dose contribution from radionuclides of uranium, thorium, radium, lead and polonium.

Table 4. The dose contribution fractions from radionuclides of uranium, thorium, radium, polonium and lead.

Sample code	Commercial name (Origin)	Dose fraction from uranium, %	Dose fraction from thorium, %	Dose fraction from radium, %	Dose fraction from polonium, %	Dose fraction from lead, %
1	Blues Aura (Umbria)	34.2	0.17	50.5	10.1	4.88
2	Egeria (Roma)	19.5	0.19	22.7	37.8	19.6
3	Guizza (Pescara)	12.2	0.01	25.2	12.2	50.4
4	Panna (Firenze)	9.25	0.05	19.4	38.1	33.1
5	Rocchetta (Perugia)	6.36	0.18	37.1	27.7	28.4
6	Lete (Caserta)	23.5	0.15	32.7	18.3	25.2
7	Vitasnella (Brescia)	21.9	0.04	33.2	26.8	18.1
8	Sangemini (Terni)	14.6	0.06	54.1	17.2	14.0
9	Brioblu Rocchetta (Perugia)	1.81	0.04	10.7	76.5	10.8
10	Vera (Padova)	16.1	0.01	6.64	21.5	55.7
11	San Benedetto (Vinece)	21.3	0.31	2.87	42.0	33.1
12	Lieve (Perugia)	9.63	0.08	66.1	9.70	14.5
13	Ferrarelle (Caserta)	3.40	0.18	66.3	24.3	5.62
14	Uliveto (Pisa)	5.93	0.65	82.3	7.20	3.25
15	Capannelle (Roma)	34.0	0.05	11.3	23.5	31.1
16	CSM tap water (Roma)	0.18	0.04	97.2	1.25	1.25
17	Magliana tap water (Roma)	18.7	0.02	66.2	4.63	10.4
Mean±SD		14.9±10.3	0.13±0.16	40.3±28.1	23.5±18.2	21.2±15.9
Range		0.18-36.0	0.01-0.65	2.87-97.2	1.25-76.5	1.25-55.7

It is shown that:

- As far as the measured radionuclides were concerned, the total doses for all the analysed drinking water were in the range of 2.81-38.5 μSv yr⁻¹ with a mean value of 11±11 μSv yr⁻¹.
- All are well below the reference level of the committed effective dose (100 µSv yr⁻¹) recommended by the WHO for drinking water.

As far as each measured radionuclide was concerned, the mean dose (μ Sv yr⁻¹) from the drinking water intake were in the order:

 $\begin{array}{lll} & 2.8 \pm 3.3 \; (^{210} Po) > 2.4 \pm 3.2 \; (^{228} Ra) > 2.1 \pm 2.1 \; (^{210} Pb) \\ &> 1.8 \pm 3.1 \; (^{226} Ra) > 0.94 \pm 1.30 \; (^{234} U) > 0.70 \pm 0.98 \\ & (^{238} U) > 0.069 \pm 0.087 \; (^{224} Ra) > 0.036 \pm 0.044 \; (^{235} U) \\ &> 0.014 \pm 0.021 \; (^{228} Th) > 0.012 \pm 0.005 \; (^{212} Pb) > \\ & 0.00035 \pm 0.00029 \; (^{230} Th) > 0.00022 \pm 0.00009 \\ & (^{232} Th). \end{array}$

5 Conclusion

- It is concluded that:
- The extraction chromatographic methods are selective, economic and accurate techniques in the field of radioanalytical analyses for environmental and biological samples, and is playing a very important role.



Thank you for your attention!