The EU Drinking Water Directive on Radioactivity. The Austrian Standard and an Ultra Low-level LSC-Approach to assure Compliance

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- European Union Council Directive 98/83/EC of 3 November 1998 on the quality of water intended for human consumption

- Indicator Parameters:
  - Tritium (100 Bq/l)
  - Total Indicative Dose (0.1 mSv/year), excluded: tritium, K-40, radon and radon decay products

- preparation of an Austrian Standard for easy decision on compliance, taking into consideration the specific situation in Austria with respect to geological situation, existing knowledge about radionuclides in (drinking) water, potential sources etc.

- methods recently developed for simple, time and labour saving determination of NORM in drinking water using liquid scintillation spectrometry

Potential Sources of Radioactive Contaminants in Austria

No operating nuclear power plant in Austria

- artificial radionuclides as sealed sources in industry or short-lived radionuclides in nuclear medicine,
- generally only NORM to be considered, unless there is reason to suspect different sources for dose relevant concentrations of other radionuclides
- NORM: highest dose factors for Ra-226 and Ra-228; Pb-210 and Po-210 excluded from calculation of “Indicative Dose”, Th-isotopes practically absent from drinking water, U-isotopes negligible
- Commission Recommendation 2001/928/Euratom to Member States to set maximum contaminant levels for Rn-222 (LIL 100-300 Bq/l, HIL 1000 Bq/l), Pb-210 (0.2 Bq/l) and Po-210 (0.1 Bq/l)
- Recommendation not implemented in Austria

The Austrian Standard ÖNORM S 5251:2005-03-01

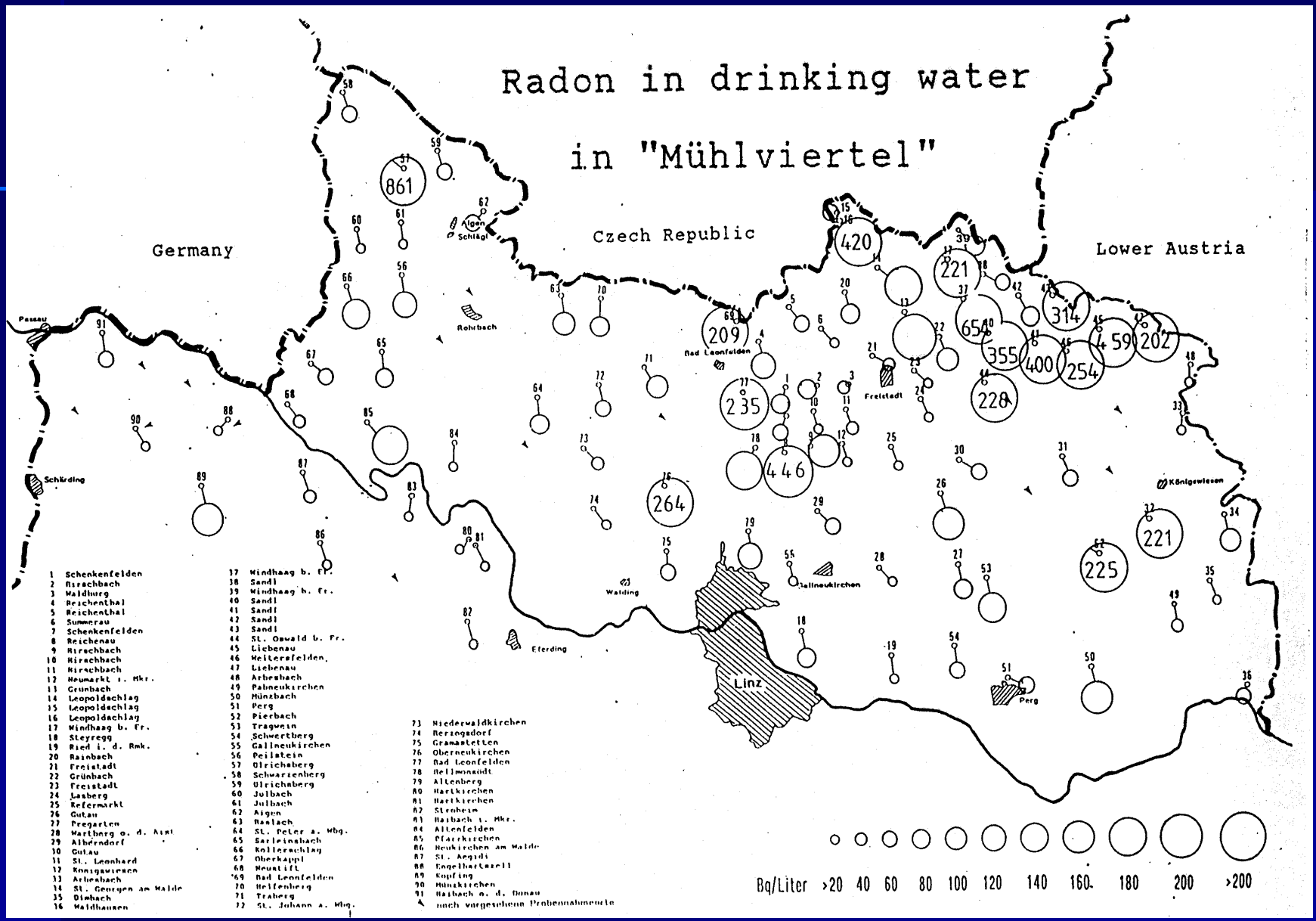
- radionuclides considered
- proof of compliance with the guideline value for the Total Indicative Dose
- measurement methods for Ra-226 and Ra-228
- calculation of total dose from drinking water
- potential contribution of other radionuclides
- sampling, inspection reporting
- examples

Strategy for decisions on monitoring

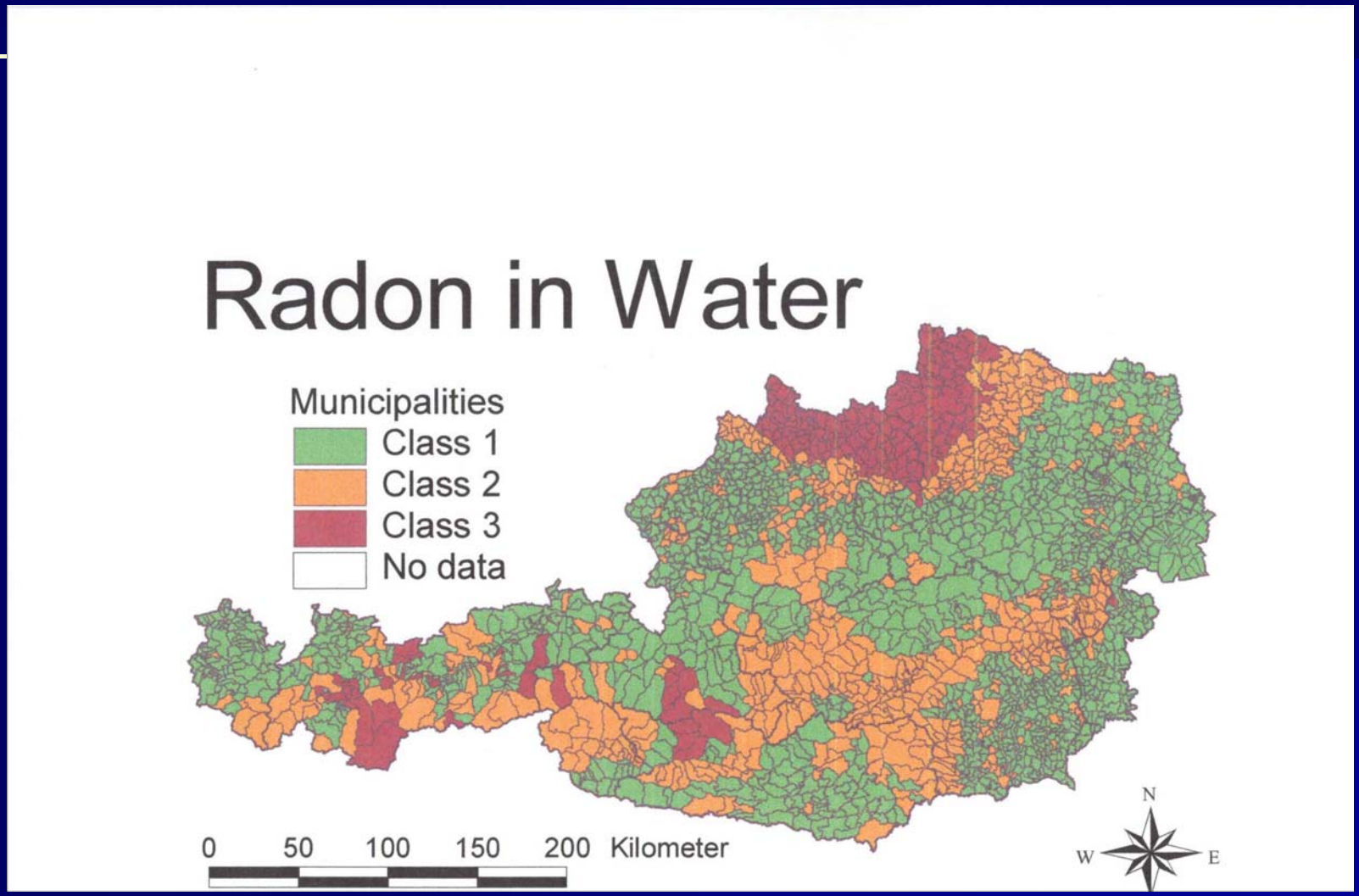
How to identify risk areas for Uranium, Radium and Radon:

- Avoid unnecessary monitoring because of costs and restrict it to areas with risk of significant levels of contaminants (encouraged by the Directive!)

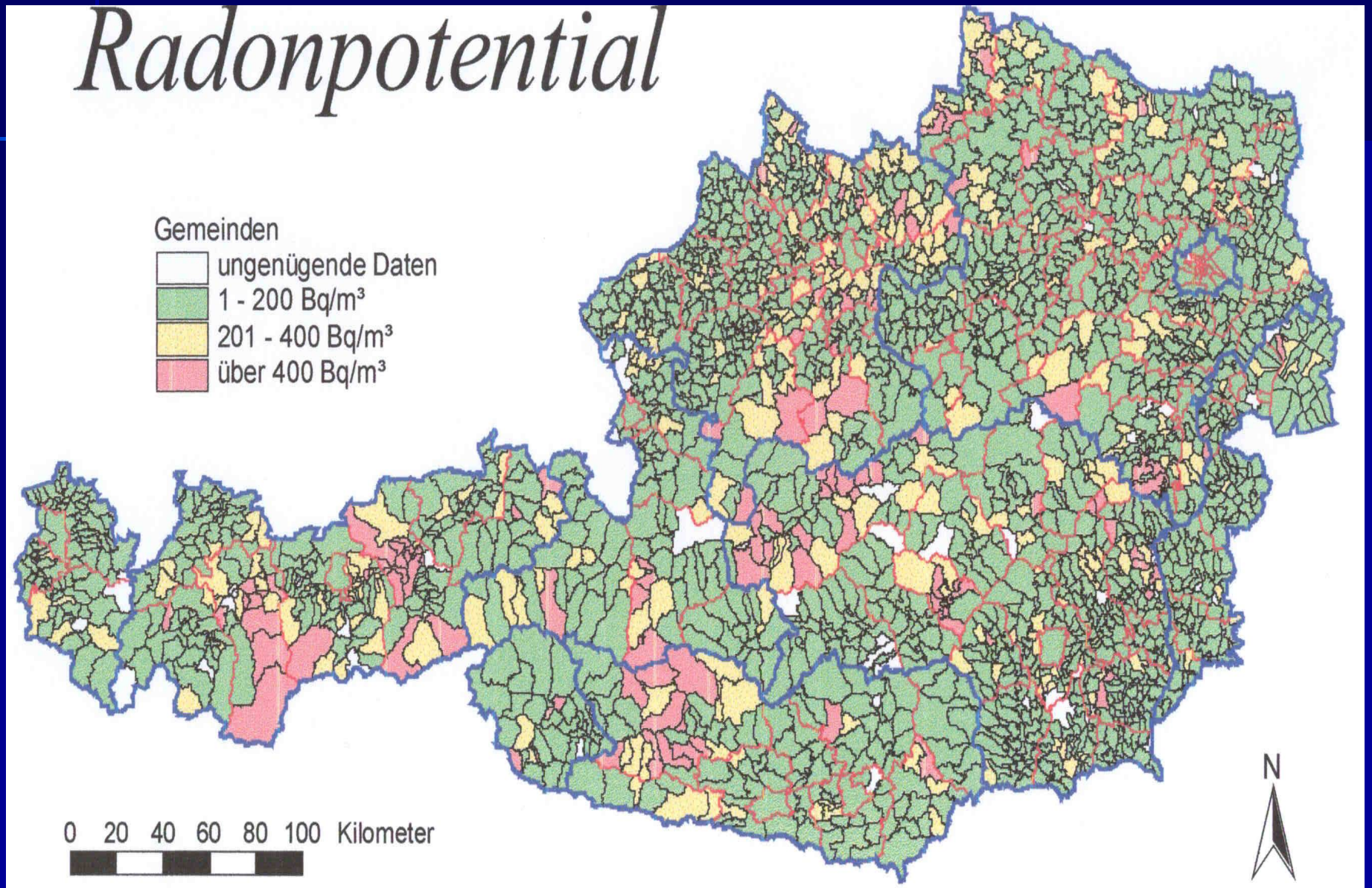
- Austrian Geochemical Atlas
  Radiation Atlas of Austria
  Measurements of radon in well, spring and groundwater since early 20th century
  Studies of Rn-222 and Ra-226 in drinking water in parts of Austria
  Radon in indoor air during 1990's


Radon in drinking water
in "Mühlviertel"
Germany
Czech Republic
Lower Austria
Passau
Schärding
Rohrbach
Bad Leonfelden
Freistadt
Königswiesen
Walding
Eferding
Linz
Hallneukirchen
Perg
861
420
221
654
314
355
400
254
459
202
209
235
446
264
228
225
1 Schenkenfelden
2 Rirachbach
3 Waldburg
4 Reichenthal
5 Reichenthal
6 Summerau
7 Schenkenfelden
8 Reichenau
9 Rirachbach
10 Rirachbach
11 Rirachbach
12 Neumarkt i. Mkr.
13 Grünbach
14 Leopoldschlag
15 Leopoldschlag
16 Leopoldschlag
17 Windhaag b. Fr.
18 Steyregg
19 Ried i. d. Rmk.
20 Rainbach
21 Freistadt
22 Grünbach
23 Freistadt
24 Lasberg
25 Reformarkt
26 Gutau
27 Pregarten
28 Wartberg o. d. Aist
29 Alberndorf
30 Gutau
31 St. Leonhard
32 Königswiesen
33 Arbesbach
34 St. Georgen am Walde
35 Dimbach
36 Waldhausen
37 Windhaag b. Fr.
38 Sandl
39 Windhaag b. Fr.
40 Sandl
41 Sandl
42 Sandl
43 Sandl
44 St. Oswald b. Fr.
45 Liebenau
46 Helterefelden.
47 Liebenau
48 Arbesbach
49 Pabneukirchen
50 Münzbach
51 Perg
52 Pierbach
53 Tragwein
54 Schwertberg
55 Gallneukirchen
56 Peilstein
57 Ulrichsberg
58 Schwarzenberg
59 Ulrichsberg
60 Julbach
61 Julbach
62 Aigen
63 Baalach
64 St. Peter a. Wbg.
65 Sarleinsbach
66 Kollerschlag
67 Oberkappel
68 Neustift
69 Bad Leonfelden
70 Helfenberg
71 Traberg
72 St. Johann a. Wbg.
73 Niederwaldkirchen
74 Herzogsdorf
75 Gramastetten
76 Oberneukirchen
77 Bad Leonfelden
78 Hellmonsödt
79 Altenberg
80 Hartkirchen
81 Hartkirchen
82 Strasheim
83 Haibach i. Mkr.
84 Altenfelden
85 Pfarrkirchen
86 Neukirchen am Walde
87 St. Aegidi
88 Engelhartszell
89 Kopfing
90 Münzkirchen
91 Haibach o. d. Donau
noch vorgesehene Probennahmeorte
Bq/Liter >20 40 60 80 100 120 140 160 180 200 >200

Measurements of radon in well, spring and groundwater since early 20th century



Radon in indoor air in Austria during 1990's



Radiotoxicity of radionuclides

The radiotoxicity (dose factors) of radionuclides given in an annex of the Radiation Protection Directive, taking their pathway, their age dependence and their physical and chemical status into consideration.

permanent ingestion of drinking water with a concentration of 0.5 Bq/l of Ra-226 (and no other radionuclides present) would result in a dose rate of 0.1 mSv/y for adults.

Age group	Annual Limit of intake, (Bq) for 0.1 mSv/y	
	^{226}Ra	^{228}Ra
Infants	21.3	3.3
1-2 years	104.2	17.5
2-7 years	161.3	29.4
7-12 years	125.0	25.6
12-17 years	66.7	18.9
adults – above 17 years	357.1	144.9

to derive drinking water concentrations for a dose of 0.1 mSv/y different annual intakes have to be considered.
especially teenagers, but also other age-groups are more vulnerable than adults for whom calculations in the ÖNORM have been done.

Tritium

- Long history of tritium measurements in Austrian precipitation, surface water and drinking water
- Since a peak in 1963/64 the tritium concentration in precipitation slowly approaches natural background level (0.6 Bq/l)
- Inspection in the vicinity of industry using tritium recommended
- Method of choice: Liquid Scintillation Spectrometry

Measurement of Rn-222, Ra-226 and Ra-228

Traditional methods

- radiochemical separation of radium, involving several precipitation and purification steps,
- counting (Ra-226 by gamma-spectrometry, by emanation technique, Ra-228 by gamma-spectrometric measurement of Ac-228 or beta measurement of separated Ac-228
- labour intensive, time consuming, costs for chemicals, skilled technicians necessary

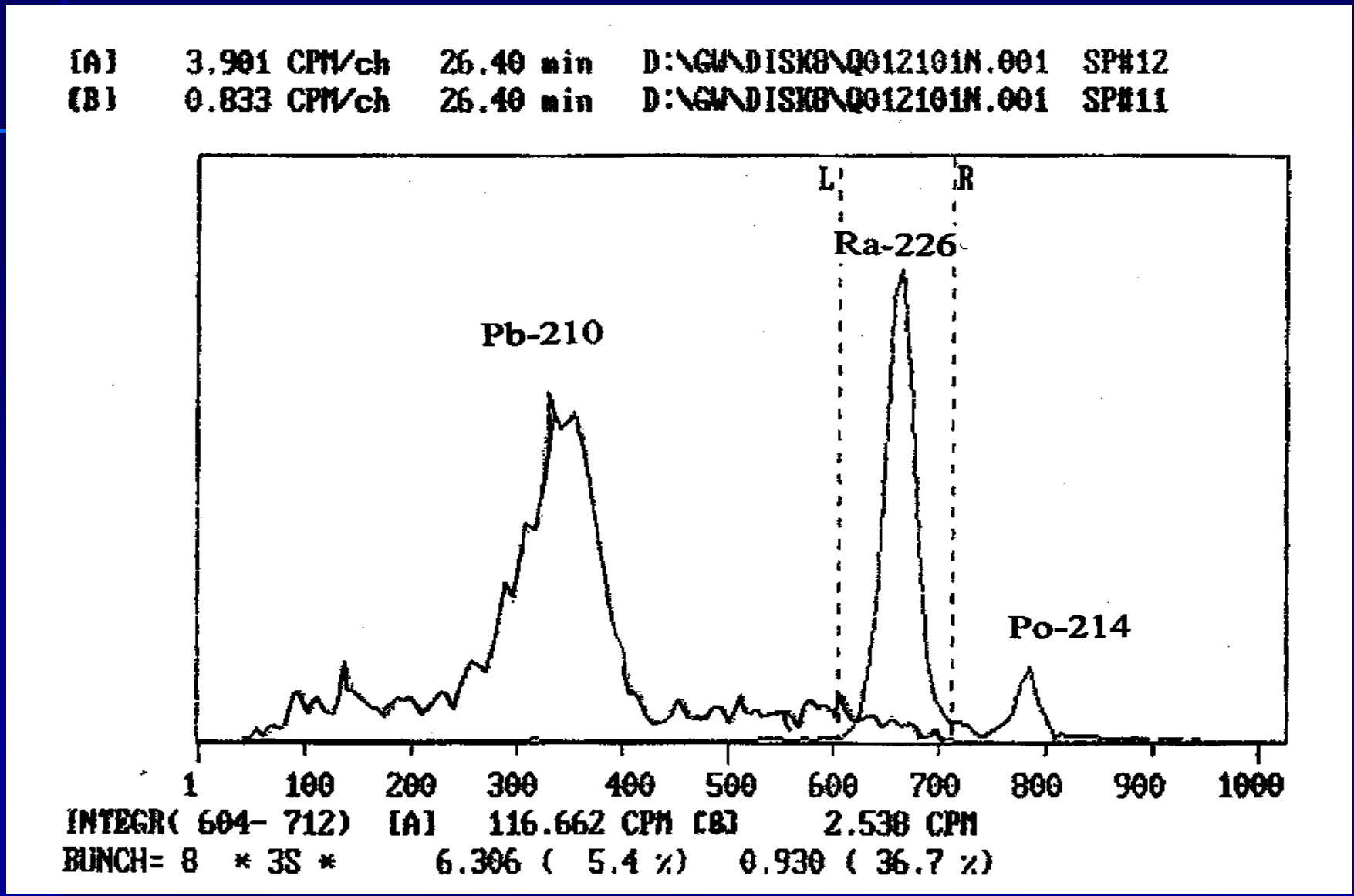
LSC methods

- determination of Rn-222 by extraction in an LSC vial into a water immiscible cocktail
- determination of Ra-226 after decay of unsupported Rn-222 in the same vial using “Quantulus”
- sample preparation for both Rn-222 and Ra-226: pipetting 10 ml of water into an LSC vial with 10 ml of cocktail, shaking, measuring for Rn-222, storing for decay of unsupported Rn-222, shaking, measuring for supported Rn-222; LLD <30 mBq/l (based on 3 sigma of background, 500 min counting time), absolutely nuclide specific
- drawback: long waiting time for establishment of equilibrium, Ra-228???
- first LSC methods for simultaneous determination of Ra-226, Ra-228 and Ra-224 introduced in the late 1980’s, including radiochemical separation

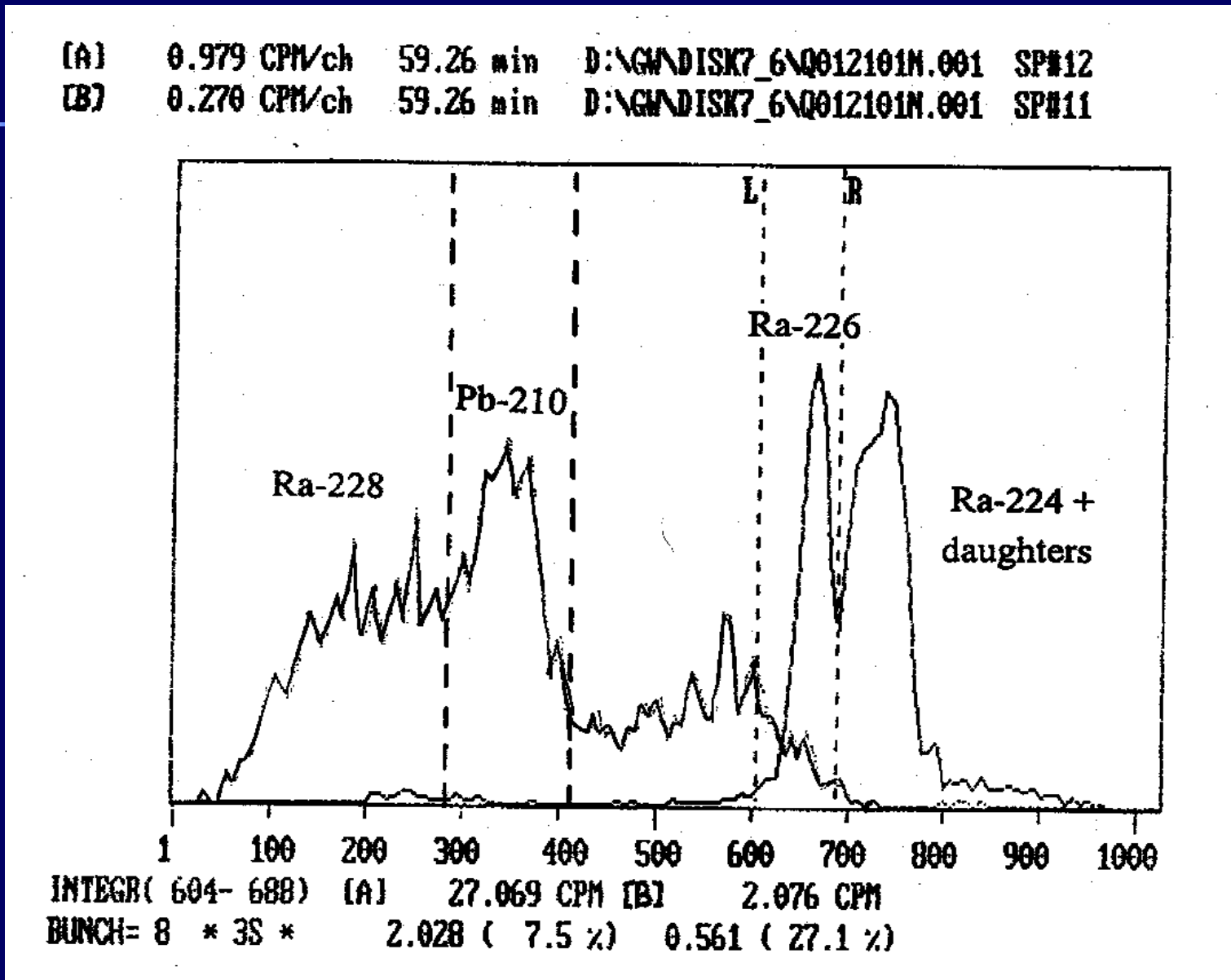
3M Empore Radium RadDisks plus LSC and alpha-beta separation

- RadDisks: crown ether impregnated, element selective inert filter material
- Sample preparation: filtering water through the disk (appr. 1 h for 1 l without suction)
- Put filter into an LSC vial, elute the adsorbed radionuclides, add LSC cocktail and measure as soon as possible using alpha-beta separation features of “Quantulus”
- Uranium and thorium are not retained, Ra-226, Ra-224, Ra-228 and Pb-210 are well retained and can be quantified
- The whole procedure takes about 2 h time and can be performed by an unskilled person; however, for evaluation a well experienced person is necessary

Spectra of a Ra-226 standard after separation on Ra-RadDisk



mixed Ra-226 + Ra-228 (together with Ra-224) standards after separation with radium RadDisk



Simplified (screening) method?

- High costs of RadDisks – cheaper method?
- Proposal: fast coprecipitation of radium isotopes with barium sulfate, dissolution in EDTA after centrifugation, mixing with cocktail, immediate measurement using alpha-beta separation
- Encouraging results at GIG: possible interferences (e.g. Th, Sr-90) negligible for drinking water

„gross Alpha“, „gross Beta“, Tritium

Draft of EU recommendation: screening for gross alpha (< 0.1Bq/l) and gross beta (<1Bq/l)

measurement of „gross alpha+beta“ used since late 80‘s by main author to detect radionuclides in waste water from nuclear research institutes and sewage plants

- used for drinking water besides nuclide specific analysis for Rn-222 and Ra-226 to control whether enhanced activities from other radionuclides detectable
- Instrument used: „Quantulus“ (Perkin-Elmer – Wallac OY, Turku, Finland): capable of alpha-beta-separation

Application for drinking water compliance:

Sample preparation: Mix 10 ml of untreated drinking water sample with 10 ml of „suitable“ cocktail

PSA-level: Determine with standards the optimum setting for the Pulse Shape Analysis Level

Count the sample with optimum instrument settings

20 different brands of Polish mineral waters purchased in Upper Silesian Supermarkets and analyzed by LSC for Ra-226, gross alpha, gross beta and tritium

For all brands concentrations of Ra-226 and Ra-228 determined by conventional radiochemical methods were known.

LLD:

counting time 400 min, basis 3 sigma of background:

Ra-226 with gross-alpha measurement: about 40 mBq/l

tritium: about 1.5 Bq/l

Ra-226 and Ra-228 after radiochemical separation: about 2 mBq/l and 20 mBq/l respectively

Results

Data for Ra-226 in excellent agreement.

Tritium results between 1.5 and 3 Bq/l – ambient concentrations and far below the 100 Bq/l limit.

gross-beta measurements: still interpretation necessary of measurements done, especially:
high concentrations of K-40 in some mineral waters disturb severely measurements of gross-beta

tritium may interfere with Ra-228 – basic problems with recommendation of gross-beta <1 Bq/l

Concerning TID a few mineral waters should be monitored carefully – depending on future legislation in Poland.

Uranium

- WHO: MPC 30 microg/l (0.370 Bq/l U-238)
- 30 microg/l of natural uranium →24 microSv/year
  0.1 mSv/year corresponds to 120 microg/l !!
- recommendation to set values for uranium on a mass basis, like in USA
- easily to be measured (e.g. ICP-MS), isotopic composition would not be needed to be known

Removal of radionuclides, radioactive waste

- Authorities may decide for removal of certain radionuclides from drinking water (→TENAWA)

Removal efficiencies for radium, lead and uranium (in %)

treatment method	Ra	Pb	U
GAC Filtration	0 – 90	30 – 99	0 – 99
Cation Exchange	95 – 98	20 – 90	-
Anion Exchange	35 – 60	20 – 70	> 95
Mixed Bed Exchange	95 – 98	20 – 90	> 95
Hydroxylapatite Filtr.	35 - 95	75 - 95	58 - 82
Reverse Osmosis and Nano Filtration	>95	>95	>95

- High external radiation doses from charcoal or ion-exchange columns might have to be considered

- Wastes like sludges, backwash water etc. might have to be classified as radioactive waste and be disposed of accordingly

Example:

- Water in Lower Austria from a bored well
- Ra-226 concentration above then recommended MPC of 0.122 Bq/m3
- Elevated concentrations of iron and manganese -> removal of Fe and Mn necessary by oxidation and precipitation
- Iron and Mn oxidehydrates are excellent scavengers for radium
- -> resulting dry residue of sludges: >20 kBq/kg Ra-226, (exemption value: 10 kBq/kg)
- -> daily amount of Ra-226 separated: > 50 kBq (exemption value: 10 kBq)
- Radioactive waste!!!!

Acknowledgements

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- This list is far from being exhaustive.