ENGLISH SUMMARY

Title: Microanalytical Investigations for the Determination of Certain Elements by Ion Chromatography and Nuclear Measurements

In this thesis it is intended to analyse bottled ground water available in local market and surface water from different locations in Egypt. This includes physical characterization, identification and determination of inorganic species and measurement of the radioactivity levels of naturally occurring nuclides in the tested samples using Filly automated ion chromatography and a number of nuclear measurements. It is subdivided into three main chapters including:

Chapter-1:

The introduction includes a historical review of chromatography, factors affecting chromatographic separations and a literature survey of the analysis of common cations and anions and previous studies for separation and determination of heavy metal ions by ion chromatography coupled with UV-Vis detection mode.

This chapter, also includes the decay schemes of naturally occurring radionuclides and short notes focusing on the distribution behaviour of radium isotopes in both surface and ground water resources. Also, a literature review of published work on determination of natural occurring radionuclides is cited.

Chapter-2:

The experimental part, defines the chemicals used and includes a map of Egypt indicating the different regions of water sampling in Siwa Oasis (Siwa, Aquasiwa, Hayat and Safi), within El-Sadat City **(Delta,** Aqua, Schweppes and Tiba), and in Western Nile Delta regions (Baraka, from near Benha City and Mineral from Belbeis City) together with surface water samples collected from Cairo, Inshas and Benha Cities. The experimental procedures used for measuring the pH, total alkalinity, electrical conductivity (EC) and the total dissolved solids (TDS) are indicated.

This chapter also includes detailed description of the ion chromatographic system used for the determination of common cations and anions and for performing analytical investigations to separate and determine different heavy metal ions in drinking water. The hyper pure germanium (HPGe) gamma spectroscopic instrument used for measuring the radioactivity levels of uranium-238 and thorium-232, and the liquid scintillation counting system (LSC) for measuring radioactivity levels of radium-226 and radium-228 are described. Chemical recovery of radium-226 and radium-228 is determined by using barium-133 as yield tracer before measuring the radioactivity levels of both radium isotopes.

Chapter-3:

This chapter includes results an discussion in three parts:

Part 1, contains both the physical characteristics and chemical composition of bottled drinking water available in the local market and the domestic surface water samples collected from different locations, giving the following mean values:

i- physical characteristics

	pH	EC, p S	TDS, mg/L	HCO3, mg/L
Western Desert, (Siwa Oasis)	8.4±0.1	253.5±40	215.5.±44	90.8±12
Western Nile Delta, (El-Sadat City)	8.3±0.2	309.5±28	267.5±61	172.7±17
Eastern Nile Delta, Benha and Belbeis	8.2±0.1	439.5±37	373±6.0	145.2±75
domestic water, Cairo, Inshas, Benha	7.6±0.2	280.3±16	227.3±13	127.7±9.6

ii-chemical composition

The mean concentration levels of common cations and anions in mg/L are:

			m^{e}	ca2+	cr	SO_4^{2-}
Western Desert, (Siwa Oasis)	34.6±3.6	20.7±1.9	10.0±1.1	10.7±3.0	27.7±4.3	18.0±6.6

Western Nile Delta, (El-Sadat City)	35.9±3.6	5.0+0.8	12.9±1.1	25.9±7.5	24.3±10.1	18.7±4.9
Eastern Nile Delta, Benha and Belbeis	48.9±7.2	5.4±0.4	19.6±5.4	39.9±1.2	89.3±45.2	50.7±5.5
domestic water, Cairo, Inshas, Benha	29.9±2.5	5.7±0.2	11.5±0.5	28.5±0.8	16.9±3.8	45.2±7.3

These data proved that the different types of tested water from ground and surface resources have characteristics within the national norms and those reported by a number of foreign countries.

Part 2, contains detailed investigations to develop rapid and reliable separation and determination of some trace heavy metal ions including lead, copper, cadmium, cobalt, zinc and nickel using automated ion chromatographic system coupled with UV-Vis detection mode. Different types of mobile phases are used, including oxalic acid, potassium oxalate, sodium oxalate and ammonium oxalate as eluents. Changes in the pH, concentration and flow rate of each eluent are studied.

i-effect of pH

The retention time of the heavy metal ions generally decreases by increasing the eluent pH. Also, changes in pH may lead to considerable change in the elution order of the separated ions. Similarity exists between potassium oxalate and sodium oxalate eluents related to the retention time and elution order of studied metal ions. The pH ranging from 4.5 to 5.0 proved to be suitable for interseparation processes.

ii-Effect of eluent concentration

The effect of eluent concentration on the retention factor and number of theoretical plates for the ion exchange separation of heavy metal ions was investigated under constant pH 4.5 and constant flow rate 0.75 ml/min. The retention factors *(k)* of the metal ions proved to decrease by increasing eluent concentrations for all types of used eluents. Also, the retention factors when using different concentrations of oxalic acid as eluent have greater values than those for ammonium oxalate, potassium oxalate and sodium oxalate eluents, which seem to be almost of the same order.

As for the number of theoretical plates N, changes in the eluent concentrations lead to minor changes in the related values. The results further shown that lead ions have the highest N values and nickel ions have lowest values. Based on the retention factor and related number of theoretical plates, the optimum eluent concentrations lie within the range (60 to 80 mM) for all eluents. Both potassium oxalate and oxalic acid eluents proved to have higher separation powers for the investigated metal ions than the other eluents.

iii-effect of eluent flow rate

The effect of eluent flow rate on the retention factors and the number of theoretical plates for ion exchange separation of investigated heavy metal ions was carried out at constant pH 4.5 and constant concentration 80 mM. The retention factors for all metal ions are insensitive to changes in eluent flow rate. The retention factors for different metal ions have the highest values when using oxalic acid as eluent than ammonium oxalate, potassium oxalate and finally sodium oxalate.

The effect of eluent flow rate on the number of theoretical plates N, showed that N decreases gradually by increasing eluent flow rate. There is no common trend to compare the N values of different mobile phases for all metal ions. In general, lead proved to have high N values, ranging from 750-1800 and nickel ions have the lowest values which range from 400-700.

In the light of these findings, three new different alternative methods are elaborated for the rapid and accurate determination of lead, copper, cadmium, cobalt, zinc and nickel using ammonium oxalate, potassium oxalate and sodium oxalate as eluent, rather than the previously reported method based on using oxalic acid as mobile phase. Also, the results proved that potassium oxalate system could be used successfully for simultaneous separation of these heavy metals ions rather than the other eluents, providing good resolution within short elution time.

Part 3, of this chapter is related to assess the radioactivity levels of naturally occurring radionuclides in bottled and surface drinking water. These radionuclides include uranium-238, thorium-232, radium-226, and radium-228.

1- The effect of physical characteristics and chemical composition of the tested water on the radioactivity level of radium revealed that:

- The radioactivity levels of radium as correlated with both the TDS and pH of tested water, give a slight decrease in the radioactivity levels of radium by increasing TDS concentrations from 150 to 400 mg/L and by increasing the pH from 7.0 to 8.5.

- The radioactivity levels of radium also give a slight positive correlation by increasing both calcium and bicarbonate concentrations in tested samples.
- The sulfate and chloride ions proved to give minor effects on the radioactivity levels of radium with concentrations ranging from 10 to 60 mg/L for sulfate and from 5.0 to 45 mg/L for chloride ions.

2- The calculated radioactivity ratios and related equilibrium of studied nuclides proved that:

- All the tested water samples have uranium-238 radioactivity levels more than those of thorium-232, and the U-238/Th-232 ratios range from 1.474 to 6.429. This may be attributed to differences in chemical behaviour of uranium species, which are known to have higher solubility and leachability, than those thorium.
- The radioactivity levels of radium-226 are almost more than those of radium-228 in all samples and Ra-226/Ra-228 ratios range from 1.203 to 5.327. This may be due to a-recoil processes in the decay series of uranium-238 to radium-226 and/or to the high levels of uranium-238 than those of thorium-232.
- The radioactivity levels of radium isotopes are higher than those of respective parents showing disequilibrium conditions in almost all tested water. This disequilibrium may be due to several factors affecting both parents and respective daughters in different manner; including differences in chemical behaviour of parents and related daughters as well as the chemical composition, salinity and pH of tested water.

3- Finally, the annual effective dose due to ingestion of drinking water was calculated for both radium-226 and radium-228 and reported with related radioactivity levels together with those of uranium-238 and thorium-232 in the following table.

radionuclide	U-238	Ra-226	Th-232	Ra-228	Ra-228	Ra-226
sample	radioactivity levels, Bq/L				annual dose, mSv/y	
	bottled drinking water from areas within the Western Desert (Siwa Oasis)					
Siwa	0.560	0.800	0.135	0.000	0.000	0.161
Aquasiwa	0.410	0.790	0.089	0.300	0.149	0.159
Hayat	0.390	0.470	0.138	0.340	0.169	0.095
Safi	0.400	1.090	0.126	0.570	0.283	0.220
mean	0.440	0.788	0.122	0.302	0.150	0.159
	bottled drinking water from areas within Western ifle Delta (EI-Sadat City)					
Delta	0.260	0.000	0.135	0.150	0.075	0.000
Aqua	0.380	1.110	0.127	0.890	0.442	0.224
Schweppes	0.340	0.830	0.114	0.620	0.343	0.167
Tiba	0.450	1.740	0.070	0.220	0.109	0.351
mean	0.360	0.920	0.112	0.487	0.242	0.488
	bottled drinking water from areas within Eastern Nile Delta (Benha and Belbeis) Cities					
Baraka	0.330	0.650	0.091	0.910	0.452	0.131
Mineral	0.230	0.220	0.156	0.640	0.318	0.044
mean	0.280	0.435	0.124	0.775	0.385	0.087
	domestic water from different Govemerates					
Cairo	0.430	2.610	0.122	0.490	0.243	0.526
Inshas	0.500	2.580	0.136	0.560	0.278	0.520
Benha	0.470	1.170	0.085	0.330	0.164	0.236
mean	0.470	2.120	0.114	0.460	0.228	0.427

4- Conclusions

- The mean radioactivity level of uranium-238 in ground and surface water is within 0.396 Bq/L. This value is lower than the reported levels in drinking water from China, Finland, France, Germany and Switzerland, and also below that included in the guidelines of WHO for uranium-238 in drinking water, which lies within 10 Bq/L [82].

- Samples collected from different resources have almost the same radioactivity levels of thorium-232, within 0.117 Bq/L, which is lower than the WHO guidelines for thorium-232 in drinking water (1.0 Bq/L). In most cases, several countries do not report reference levels of thorium-232, see Table 3.17.

-The empirical equation first formulated in the present work, introduced a new trend for the determination of the radioactivity levels of both radium-226 and radium-228 in the presence of each other by liquid scintillation counting. Spectral interference of (alpha emitting) radium-

228 daughters in the a-energy window of radium-226 and those of (beta emitting) radium-226 daughters in the counting n-region of radium-228 are prevented or almost reduced.

- The mean annual effective dose for bottled ground water, based on the radioactivity levels of radium-226, is almost around 0.144 mSv/y comparable to the recommended limit reported by WHO, being 0.1 mSv/y. For both ground water and surface water, the mean effective dose is about 0.215 mS/y, which is 2.15 times higher than the WHO limit for drinking water. The mean annual effective doses received from ingestion of both ground and surface waters are still lower than those reported for drinking water in several countries including Finland, Germany, Spain and Italy.

- The mean annual effective doses from both surface and ground water lie within 0.251 mSv/y, a value which is higher than the WHO limit (0.1 mSv/y), but lower than maximum reported value of 0.287 mSv/y for drinking water in a number of foreign countries.

- Despite the fact that, some tested samples showed elevated levels of radioactivity for both radium-226 and radium-228, yet the mean radioactivity level is still less than what is reported for drinking water in several other countries and is matching with the typical range 0.2 to 0.8 mSv/y for ingested food and drinking water reported by UNSCEAR [103].