

POTENTIOMETRIC DETERMINATION OF FLUORIDE AND IODIDE IN NATURAL AND PROCESSED WATERS OF BAHRAIN USING ION-SELECTIVE ELECTRODES

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Abstract—To assess the natural availability of fluoride and iodide in Bahrain, natural and processed waters which included ground water, tap waters, Adari Lake water and streams and waters from reverse osmosis (RO), ion-exchange (IE), multistage flash desalination (MSF) and solar desalination (SD) plants, in addition to blended waters, were monitored for 3 months (Oct.–Dec. 1985). The fluoride ion concentration ranges from 0.45 to $1.51 \pm 0.26 \text{ mg dm}^{-3}$ in natural waters; 0.003 to $0.33 \pm 0.016 \text{ mg dm}^{-3}$ in the processed waters and 0.15 to $0.24 \pm 0.095 \text{ mg dm}^{-3}$ in the blended waters. As for the iodide ion, concentration ranges from 0.02 to $1.08 \pm 0.07 \text{ mg dm}^{-3}$ in natural waters; 0.01 to $0.02 \pm 0.002 \text{ mg dm}^{-3}$ in both processed and blended water.

Key words—fluoride, iodide, natural water, processed water, ground water, blended water, toxicity of fluoride, iodine deficiency, ion selective electrode, brackish water, COD

INTRODUCTION

Water has always been vital for man's existence. No matter what the purpose for which water is required, it has long been recognized that its suitability for that purpose can be affected by other substances (Wilson, 1984). Among these substances are fluoride and iodide ions.

Fluoride in drinking and natural water is important in consideration of health aspects of the population. Publications on this subject (Powers, 1952; CRC, 1973) show how close together positive and negative effects of fluoride content in drinking water may be: on one hand, it was found that dental caries are less frequent by 58% in a place with high fluoride concentration ($1.8 \text{ mg F}^{-} \text{ dm}^{-3}$) when compared with the population from a neighbouring community supplied with low-fluoride drinking water ($0.5 \text{ mg F}^{-} \text{ dm}^{-3}$). On the other hand, fluoride-associated enamel hypoplasia was observed within the same group which was clearly elevated (74%) in the place of high fluoride concentration against 33% on the comparative group, (Lelyveld and Zoeteman, 1981). Generally speaking, fluoride is considered a nutritionally essential element because it increases growth rates when added to diets as fluoride compounds. However, it can be toxic in high concentrations resulting in decline of appetite, slow growth and bone and joint abnormalities (McDonald *et al.*, 1980). The normal drinking water concentration is 1 mg dm^{-3} (APHA, 1980). As for iodide, it is a long established fact that everywhere in the world, endemic goitre occurs more commonly in certain geographic areas. Iodide

deficiency is the most frequent cause of euthyroid goitre.

Normal ground waters contain between 0.01 and $20 \mu\text{g I}^{-} \text{ dm}^{-3}$ while in drinking water the concentration varies between 0.5 and $15 \mu\text{g dm}^{-3}$ (Lelyveld and Zoeteman, 1981). Among the techniques used for the determination of F^{-} and I^{-} in water samples is potentiometry using ion-selective electrodes. Fluoride assessment in sea and potable waters, the parameters which affect halide determination using selective electrodes, continuous analysis and control of fluoride using analysers and automated determination of fluoride by direct method were reported (APHA, 1980; Zeinalova and Senyanin, 1975; Warner, 1971a, b; Rix *et al.*, 1976). The determination of halide concentrations in the water started when their limit in drinking water was standardized. The results showed that ion-selective electrode techniques are less labour and time consuming with reasonable percentage error due to interference. This study was conducted in order to assess the natural availability of the F^{-} and I^{-} ions in Bahrain waters both natural and processed.

This is due to the fact that the isles of Bahrain are with limited water resources, as the salinity of the drinking water mainly from ground resources has reached an unpalatable degree. The aquifer has almost reached the drainage line where sea water has started to mix with the brackish water. Due to this fact, the authority started in the seventies and early eighties to capitalize on the desalination of sea water both using MSF and RO desalination processes to meet the growing demands for water consumption in this archipelago. To our knowledge, no work concerning these two vital ions has been published.

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EXPERIMENTAL PROCEDURES

Apparatus

Potentials between a 99-09 LaF₃ electrode (Ingold F⁻ sensitive Electrode) and a saturated Ingold Calomel Electrode for F⁻ determination were measured on a Crison Digilab 517 meter. For I⁻ determination, potentials between a 94-53 AgI/AgS electrode (Ingold I⁻ sensitive Electrode) and a saturated Ingold Calomel Electrode were measured on a Crison Digilab 517 meter. The pH of the water samples was measured on a PTI-6 Universal digital pH meter. The conductivity of the water samples was also measured using a Crison Conductometer 525. Statistical analyses were carried out using Apple II plus computer using a standard deviation software programme.

Sampling

Samples were collected in clean plastic bottles which were rinsed by the same water several times during each sampling. Samples were simply taken from taps, water pumps or by immersing a bottle under the water surface as in lakes and springs.

Reagents

Double distilled water was prepared in the Department of Chemistry by distilling the tap water using a Fi-stream Water Still (Fisons). The distillate was redistilled using Autostill-Autofour W.S. system Jencons (Scientific Field Ltd). The final products were collected and stored in plastic containers. This pure water, which had a conductivity of $1.2 \mu\text{S cm}^{-1}$, was used for washing, rinsing and dilution throughout this study.

TISAB II. In 500 cm³ distilled water, 57 cm³ glacial acetic acid (Analar BDH), 58 g NaCl (Technical BDH) and 4 g CDTA-TCI-GR *trans*-1,2-cyclohexanediamine tetracetic acid monohydrate (Analar) were dissolved. The pH was adjusted between 5.0–5.5 with 5 M NaOH (Technical BDH) and diluted to 1 dm³.

I⁻ ISA. Five M NaNO₃ was prepared by dissolving 42.5 g Analar grade (Fluka) NaNO₃ in 100 cm³ distilled water.

Reference electrode filling solution. One M KNO₃ technical grade BDH.

Standard solutions. Standard 0.1 M solutions of F⁻ and I⁻ were prepared from NaF (BDH) and NaI (Puriss, Fluka).

Methods

For F⁻ determination: (Warner, 1971a; Ingold, 1978). Samples were mixed with TISAB(II) in the ratio of 1 cm³ of sample to 1 cm³ of buffer at least an hour before analysis to allow for slow Al(III) complexing which was assumed to be low in the water samples analysed. Usually 50 cm³ of the water sample were taken for analysis, placed in a 100 cm³ plastic beaker and stirred with a Teflon stirring bar after the insertion of the electrode to prevent bubble formation. In general, unchanging potentials were observed within a few minutes.

For I⁻ determination: (Warner, 1971a; Ingold, 1978). Samples were mixed with ISA in the ratio of 50 cm³ of sample to 1 cm³ of buffer at least an hour before analysis to keep a constant background ionic strength relative to variable concentrations of halide. Usually, 100 cm³ of the water sample were taken for analysis, placed in a 100 cm³ beaker and stirred with a Teflon stirring bar after the insertion of the electrodes to prevent formation of bubbles. In general, unchanging potentials were observed within 5–20 min.

pH and conductivity

For each water sample throughout the analysis, the pH and conductivity were measured to see any correlation with the obtained F⁻ and I⁻ concentrations.

COD of the water

As most of the analysed waters are brackish, the best

method (Golterman, 1970) to suit this determination is the following: to a 50 cm³ water sample in an Erlenmeyer flask, 5 cm³ of 0.1 M KMnO₄ were added. The flask was heated in a boiling water bath for 1 h. Then 5 cm³ of 10% KI followed by 10 cm³ of 2 M H₂SO₄ were added to the flask after cooling. Then it was titrated with 0.1 M Na₂S₂O₃ using starch as an indicator.

RESULTS AND DISCUSSION

Precision of F⁻ determination is affected by pH, ionic strength and the presence of microcomponents in the solution like Al(III), Fe(III) and organic matter (Golterman, 1970). These both affect the state of the test ions in solution and the membrane electrodes. Iodide, however, seems to complex with Cu(II), Fe(II), organic matter, etc.; organic matter was found to be in most of the water samples (Table 1).

Referring to Table 1, it is interesting to see that even the distillate product waters contain especially high chemical oxygen demand (COD). This can be attributed to either chemical doses input; such as those used as descaler in multistage flash desalination plant (MSF) (a polymer organic polyphosphate is widely used); or it is due to organic fouling by the resin as in an ion-exchange plant. The analyses of F⁻ and I⁻ were conducted using direct potentiometric method. The results seem to be consistent because of the low variance and standard deviation obtained. The F⁻ concentration (Table 1) in the processed and blended water is low compared with the international standard (WHO, 1963) for drinking waters (1.0–1.5 mg dm⁻³). As for I⁻ content (Table 1) the blended and the processed drinking waters are within the standard normal concentration, i.e. 1.0×10^{-5} – 2.0×10^{-2} mg dm⁻³. As mentioned earlier, the major parameters which affect fluoride and iodide determination are pH, macro-ions like HCO₃⁻, Cl⁻, NO₃⁻, SO₄²⁻, Na⁺, K⁺, Ca²⁺, etc.; and micro-ions like Al(III), Fe(III), Cu(II), Zn(II), etc. (Zeinalova and Senyavin, 1975). The pH mainly affects the F⁻ if it is not within the range of 5–8, a condition obtained using TISAB(II), while iodide is not affected over the wide range of pH 3–12.

This environmental analytical study showed that the water source of both fluoride and iodide ions were considerably lower (post desalination) in the blended (drinking water) as well as the deionized water as these are the main sources of public drinking water on the isles of Bahrain (Table 1), compared to predesalination of the ground waters which were used quite extensively in the seventies.

Although the concentration of the fluoride ion could be regarded as rather low compared to the international standard (1.0–1.5 mg dm⁻³), it is the iodide (which varies from place to place in the world) which is hard to compare. The iodine content in surface waters is < 106 ppm from rocks of aquiferous complex of the Turkenen platform (Geogol, 1983) and in artesian basins and mineral waters in central Asia it ranges between 3–20 mg dm⁻³ (Bender,

Table 1. Fluoride, iodide, conductivity, pH and COD determination in natural and processed waters

Sample	Fluoride				Iodide				Conductivity				pH (25°C)				COD
	Mean (mg dm ⁻³)	Variance	Deviation	% Error 90% confidence	Mean (mg dm ⁻³)	Variance	Deviation	% Error 90% confidence	Mean μS cm ⁻¹ (× 10 ³)	Variance	Deviation	% Error 90% confidence	Mean	Variance	Deviation	% Error 90% confidence	
Natural water																	
Naim	1.13	0.04	0.21	12.4	0.07	0.001	0.03	28.6	5.13	0.15	0.38	4.3	7.65	0.04	0.21	1.6	1.6
(Al-Hussaini)	0.84	0.04	0.21	14.3	0.02	0.00	0.01	33.4	3.71	0.01	0.09	1.3	7.56	0.07	0.26	2.0	3.2
Karbadad ground	1.43	0.08	0.28	11.9	0.49	0.02	0.13	16.3	10.62	3.06	1.75	9.5	7.65	0.03	0.17	1.3	4.8
Adari 1 stream	1.50	0.08	0.29	12.0	0.52	0.01	0.11	11.5	10.61	3.17	1.78	9.7	7.65	0.02	0.14	1.1	1.6
Adari 2 stream	1.51	0.07	0.27	11.3	0.49	0.01	0.11	16.3	10.63	3.35	1.83	10.0	7.59	0.05	0.22	1.7	0.0
Adari 3 stream	1.37	0.14	0.38	17.5	0.65	0.01	0.08	7.7	14.21	2.11	1.45	5.9	7.61	0.03	0.17	1.3	0.0
Adari 4 stream	0.79	0.02	0.15	11.4	0.12	0.00	0.03	16.7	7.87	0.35	0.59	4.3	7.34	0.04	0.21	1.6	1.6
Adari centre lake	0.59	0.06	0.25	30.5	0.02	0.00	0.01	30.5	3.13	2.51	1.58	2.9	7.63	0.05	0.23	1.7	1.6
Hooro ground	0.90	0.04	0.20	13.3	0.06	0.00	0.02	16.7	4.59	0.01	0.08	1.1	7.68	0.05	0.23	1.7	1.6
Salmaniya ground																	
West Riffa																	
ground	0.88	0.04	0.20	14.8	0.02	0.00	0.01	35.0	3.58	0.14	0.38	6.1	7.62	0.24	0.49	3.7	3.2
Blended water																	
Mahooz (tap)	0.17	2.39	0.05	17.6	0.01	0.00	0.00	1.85	1.13	0.07	0.26	13.3	7.69	0.01	0.11	0.8	0.0
Muharraq 209																	
(tap)	0.24	0.01	0.07	20.8	0.02	0.00	0.01	30.7	1.59	0.01	0.11	4.3	7.98	0.09	0.29	2.1	3.2
Hooro blended	0.19	0.004	0.06	21.1	0.01	0.00	0.00	0.00	1.48	0.07	0.27	0.1	7.66	0.06	0.25	1.8	1.6
Salmaniya blended	0.16	0.01	0.08	31.3	0.01	0.00	0.003	20.5	1.53	0.60	0.78	23.3	7.71	0.06	0.25	1.8	1.6
W. Riffa blended	0.15	0.02	0.13	53.3	0.01	0.00	0.01	33.7	1.20	0.08	0.28	10.1	7.99	0.06	0.24	1.8	3.2
Processed water																	
MSF (multistage																	
flash desalination																	
process) seawater																	
inlet	0.93	0.09	0.29	19.4	1.08	0.02	0.13	7.4	58.38	0.92	0.96	0.95	8.02	0.10	0.32	2.4	1.6
Distillate product	0.003	0.0	0.00	47.7	0.01	0.00	0.003	18.3	0.03	0.00	0.01	20.0	7.11	0.41	0.64	5.2	6.4
RO (reverse																	
osmosis																	
desalination																	
process) brackish																	
well water inlet	0.94	0.06	0.25	17.0	0.73	0.02	0.16	13.6	17.85	0.08	0.29	0.95	7.12	0.06	0.25	2.0	1.6
RO brine	2.12	0.41	0.64	18.7	1.04	0.33	0.58	36.5	45.52	1.45	1.20	1.0	6.93	0.13	0.36	3.0	1.6
RO product	0.03	0.00	0.01	20.0	0.016	0.00	0.00	15.0	0.35	0.01	0.96	17.1	6.76	0.35	0.59	5.0	0.0
Product water	0.05	0.00	0.03	38.0	0.01	0.00	0.00	7.6	0.44	0.01	0.09	11.4	8.08	0.52	0.72	5.2	1.6
IE (ion-exchange																	
process) brackish																	
well water inlet	0.92	0.07	0.26	17.4	0.02	0.00	0.01	35.0	4.06	0.005	0.07	0.99	7.76	0.08	0.26	1.9	9.6
Deionized																	
water outlet	0.33	0.004	0.07	12.1	0.01	0.00	0.003	18.3	0.69	0.002	0.04	2.9	7.55	0.13	0.36	2.8	7.6
SD (solar																	
desalination																	
process)	0.002	0.00	0.001	24.1	0.01	0.00	0.00	0.00	0.01	0.00	0.004	50.0	7.13	0.57	0.75	6.0	—

1968). In potable water from some zones of the province of Granada in Spain the iodide levels were 250–6300 mg dm⁻³; however, the level of iodide in the drinking water is generally below the minimum value necessary for a proper diet (Muros *et al.*, 1985). However, in some Malawi ground water and piped water supplies the iodide levels were very low <4.2 mg dm⁻³ with some exceptions at 0.028–0.034 mg dm⁻³ (Guta and Roger, 1982).

CONCLUSION

One could argue that although the water resources are very valuable in a desert climate like Bahrain, the use of the desalination processes of different types has reduced considerably the concentration of these valuable nutritional ions. Even after blending the desalinated water products with ground water, the blended (drinking water) lost some of the fluoride and iodide concentration compared to that of predesalination. These low levels of the two ions could be enriched either by other sources of nutrition to prevent the malfunction of the deficiency of the nutritional ions or by simply adding some salts of these ions to bring their levels to the international standard.

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REFERENCES

- APHA (1980) *Standard Methods for the Examination of Water and Wastewater*, 15th edition, pp. 334–337, 342. American Public Health Association, Washington, D.C.
- Beder B. A. (1963) Artesian basins and mineral and thermal waters in central Asia and some problems of mineral waters formation. Tr. Nanch-Tekh. Soveshch Gridrogeol. *Inzh. Geol.* (Pub. 1968) 72–79 (in Russian).
- CRC (1973) *Handbook of Environmental Control*, Vol. III. Water Supply Treatment.
- Geogol S. B. (1983) Geochemistry of iodine in surface waters of the Turkinen platform. *Geol. Razved.* **26**, 79–83 (in Russian).
- Golterman H. L. (1970) Methods for chemical analysis of fresh waters. *IBP Handbook No. 8*, Chap. 7, p. 107. Revised second printing.
- Guta C. W. and Roger N. E. (1982) Iodide in some Malawian ground waters and piped water supplies. *Luso* **3**, 89–94.
- Ingold W. Ag. (1978) Manual for F⁻ determination using Ingold solid state fluoride-ion electrode. Orion Research incorporated form IM94–29/8710.
- Lelyveld H. V. and Zoeteman B. C. J. (1981) *The Science of the Total Environment*. Elsevier, Amsterdam.
- McDonald P., Edwards R. A. and Greenhalgh J. F. D. (1980) *Animal Nutrition*, 3rd edition, pp. 107–108.
- Muros Guadix P., Olea F. M. and Garcia-Villanova R. (1984) Determination of iodide in drinkable water from some zones of the province of Granada with ion-selective electrode. *Ann. Bromat.* **36**, 77–81.
- Powers L. (1952) *N.W. Med.* **15**, 115.
- Rix C. J., Bond A. M. and Smith J. D. (1976) Direct determination of fluoride in sea water with a fluoride selective ion electrode by a method of standard additions. *Analyt. Chem.* **48**, 1236–1239.
- Warner T. B. (1971a) Electrode determination of fluoride in ILL-characterized natural waters. *Wat. Res.* **5**, 459–465.
- Warner T. B. (1971b) Natural fluoride content of sea water. *Deep-Sea Res.* **18**, 1255–1263.
- Wilson A. L. (1984) *The Chemical Analysis of Water, General Principle and Techniques*, p. 1. The Society for Analytical Chemistry.
- World Health Organization (1963) *International Standards for Drinking Water*, 2nd edition. World Health Organization, Geneva.
- Zeinalova E. A. and Senyavin M. M. (1975) Use of ion-selective electrodes to determine fluorides, chlorides, and iodides in natural water. Translated from *Zh. analit. Khim.* **30**, 2207–2212.