

MONITORING OF FLUORIDE AND IODIDE LEVELS IN DRINKING WATER USING ION SELECTIVE ELECTRODES

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Fluoride and iodide, the most important constituents of drinking water are essential as well as toxic depending on their levels. For their analysis in water mostly ion-selective electrodes, spectrophotometry, titrimetry and coulometry etc; have been used and literature has been briefly reviewed. Ion-selective electrodes offer an efficient method for the measurement of the two halides and were mostly used during this work. Fabrication of these electrodes is briefly described. Comparison of results obtained by ion selective electrode and coulometry is given. Recoveries of the added fluoride ions from the samples were good. A large number of water samples from Rawalpindi-Islamabad area were analyzed for fluoride and iodide. Levels of fluoride and iodide from two main water reservoirs of Rawalpindi and Islamabad are reported before and after treatment. Both surface and ground water samples were analyzed and results are compared and discussed. Some samples from northern areas were also analyzed for iodide and fluoride and compared. Intake of fluoride and iodide from water of different areas is also compared. Water samples, which caused bone deformation in certain areas in Punjab due to excess fluoride, were also analyzed for fluoride and results are presented.

Keywords: Fluoride, Iodide, Toxicity, Ion selective electrodes, Water analysis

1. Introduction

Trace elements, which enter the body, play an important role in maintaining human health [1-2]. To avoid any health hazards monitoring of food for the levels of the trace elements is very important [3]. Water has special significance because of its large consumption and better uptake metabolism of trace elements from their ionic state in water. Monitoring of water sources and drinking water for different trace elements has become very important [4-5]. Fluorine and iodine are important essential elements. Fluorine is known as constituent of bones, teeth, soft tissues and body fluids. A high incidence of caries in humans has been correlated by many investigators to a low fluoride intake. A low fluoride intake is connected with a progressive decline of fertility in mice. Excessive intake of fluorine results in fluorosis [6-7]. Higher levels of fluoride may cause bone softening and deformation and this happened in certain areas of Punjab. Thus it is necessary to maintain optimum level of fluoride in water, which is around 1 µg/ml. In many countries fluoride is added into the main water supplies and this process is called fluoridation. Iodine deficiency is

well known for goiter. In the northern mountainous regions in Pakistan where there is a deficiency of iodine in drinking water, goiter cases are common. Iodine deficiency causes other health problems also [2]. As a matter of policy the Government of Pakistan provides and encourages the use of iodized salt. Iodine is well known for its requirement by the body for the synthesis of the thyroid hormones thyroxine and triiodothyroxine. A high intake of iodine does not generally cause problems as it is easily excreted by the kidney [7]. Both food and drinking water are important sources of dietary fluorine and iodine. Water due to its large consumption by human being needs its quality control for fluorine and iodine to see the toxicity or deficiency problems [2,7-9].

Different analytical methods are available for the analysis of fluoride and iodide in water [10-13]. Among the different analytical methods ion-selective electrodes are cost-effective, efficient and reliable [14-17]. During the work methods based on ion-selective electrode were worked out for the analysis of fluoride and iodide in water. Drinking water samples from Rawalpindi – Islamabad areas and from northern areas were also analysed.

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Results about the levels of fluoride and iodide in water samples are presented, compared and discussed.

2. Experimental

2.1. Instruments/Apparatus

Potentiograph model E536 and pH meter model 605 from Metrohm, Switzerland were used for potential measurement of the electrodes. Ion-selective electrodes used were of Metrohm and Orion research USA. Coulometric system used for the measurement of halide ions was a model 173 Potentiostat / Galvanostat with model 179 Digital Coulometer from Princeton Applied Research, USA. All the glassware used were of Pyrex.

2.2. Reagents

Stock solutions of fluoride and iodide (1000 mg/l) were prepared by dissolving sodium fluoride and sodium iodide (E. Merck) in doubly deionized water. Standard solutions for calibration curves were prepared by appropriate dilutions of the stock solution. NaCl, glacial acetic acid, sodium citrate, NaOH, KNO₃, sodium acetate, Complex IV (CDTA, trans 1,2-Diamino-cyclohexane N,N,N',N' tetraacetic acid) all from E. Merck were used to prepare total ionic adjustment buffers. Doubly deionized water was used throughout this work.

2.3. Sampling and sample preparation

Standard procedures were used for sampling and sample preparation [4]. Water samples were collected in precleaned polyethylene bottles. Bottles were washed with water to be collected two to three times before sampling. Samples were analysed immediately after collection otherwise the sample bottles were stored at -20 °C and were taken out, thawed and analyzed. Storage of samples at low temperatures is necessary to avoid any losses due to volatilization.

2.4. Procedure

For fluoride analysis, different total ionic strength adjustment buffers (TISAB) were prepared and used. To approximately 500 ml of distilled water in a 1000 ml beaker 57ml of glacial acetic acid, 58 g of NaCl and 0.3 g of sodium citrate were added and dissolved at room temperature. Adjust the pH of the solution between 5 and 5.5 with 5 N NaOH and make up the volume to 1 litre. Instead of sodium citrate 5 g of complex IV (CDTA, trans 1,2- diamino cyclo hexane N, N, N', N' -tetracetic acid) may be used. Other ionic strength adjusters

(ISA) are also used e.g. 2 M KNO₃ solution for neutral samples and 2 M CH₃COONa for alkaline samples. Ionic adjustment buffers are mixed with sample in 1:1 ratio prior to measurement for fluoride.

For the analysis of Iodide in drinking water, no specific treatment is required. Water samples can directly be measured using standard calibration curves or standard addition methods. Blanks were measured using deionized water to subtract any background levels of ions. Normally three samples were collected from each site and each sample was measured at least thrice and average values were calculated.

3. Results and Discussions

Ion selective electrodes are being used extensively for the analysis of different anions and cations in general and fluoride and iodide in particular. Applications of ion selective electrodes and sensors have been widely reviewed [18-23]. Different ionophores have been used [24] for fluoride but commonly used fluoride ion selective electrodes are LaF₃ crystal based [25-27] for the analysis of water [28,29]. Work has been reported about the use of different buffer systems for fluoride measurement in water [29]. Studies have been carried out about the optimization and development of electrodes including doping of LaF₃ [30] use of conducting polymers [31] self-plasticizers [32] and development in electrochemical aspects [33-35]. Methods have also been worked out for the analysis of iodide (36-37). Flow injection methods have also been used for the analysis of fluoride and iodide [38-40].

Fluoride and iodide were analysed in the present case by coulometry and ion-selective electrodes. Details about the coulometric method have been partially reported [41]. The cell for the determination of the concentration of an ion, Mⁿ⁺, with an ion-electrode is shown below:

External Reference Electrode	Solution to be analysed [M ⁿ⁺] = C	Membrane	Internal standard solution [M ⁿ⁺] = C _s	Internal reference electrode
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The measurement of the potential between two reference electrodes allows the determination of the membrane potential caused by difference in the concentration of Mⁿ⁺ ion between the analyte and the internal reference solution. The membrane potential E_M may be given by

$$E_M = 2.303RT/nF \log (C/C_s)$$

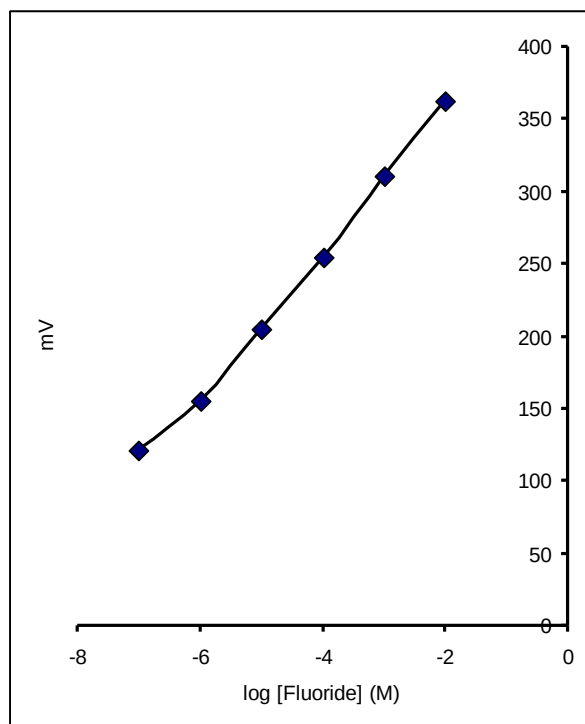


Figure 1. Calibration curve of Fluoride.

where C and C_s are the concentrations of M^{n+} in the analyte and the internal reference solution respectively. The cell potential is given by

$$E_{\text{cell}} = E_M + \Delta E_{\text{Ref}}$$

$\Delta E_{\text{Ref}} = 0$, if identical reference electrodes are used

Since C_s is a constant, the equation for the cell potential can be simplified to

$$E_{\text{cell}} = \text{constant} + 2.303 \left(\frac{RT}{nF} \right) \log C$$

This equation enables concentration to be determined from a plot of E_{cell} versus $\log C$. A linear plot is expected with a slope of $60/n$ millivolts.

Fluoride and iodide ion-selective electrodes are solid-state membrane electrodes. The membrane thickness is usually greater than 3mm for single crystal pressed pellet electrodes. The fluoride electrode consists of a LaF_3 single crystal doped with EuF_2 to lower the ohmic resistance of the membrane. The unusual selectivity of the electrode rests on the fact that only fluoride ions are involved in the phase transfer. The sensor single crystal LaF_3 membrane is in contact with an internal

reference electrolyte. The crystal acts as an ionic conductor in which only fluoride ions can migrate. The internal reference electrolyte has fixed fluoride and chloride concentrations. The linear working range of the electrode is from about 10^{-7} M to 1 M of fluoride. When working at the lower end of the concentration range great care should be taken to avoid any errors. The linear part of the curve for the fluoride electrode (Fig.1) has a slope of 49.2 mV and value of r^2 is 0.995. At the lower side of the concentration the linearity of the curve is not that good. After certain time during usage of electrodes the slope of the curve shifts a little from its expected slope of 60/mV but linearity of the curve is not affected. Possible interferences during the measurement of fluoride may be those of hydroxide ions [14] in basic solutions and hydrogen ions in acid solutions form undissociated complexes such as HF and HF_2^- and fluoride does not remain in free state, which is necessary for its accurate measurement. Both interferences can be easily eliminated if the pH of the sample is maintained between 5 to 5.5 and total ionic adjustment buffers are added. Performance of the fluoride ion selective electrode is extraordinarily good and gives reproducible and accurate results.

The iodide ion-selective electrode consists of a compressed pellet of silver sulfide and silver

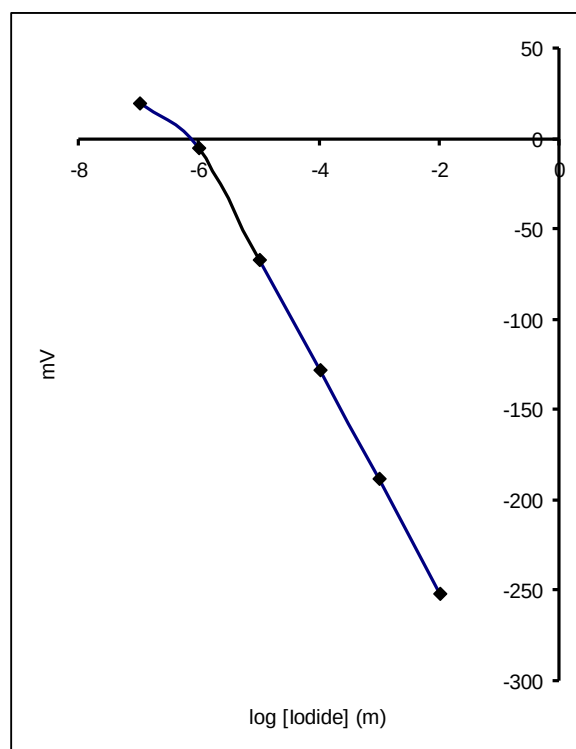


Figure 2. Calibration curve of Iodide.

iodide. Due to its large compressibility, silver sulfide serves as a base material for halide as well as for metal electrodes. About 30% of the corresponding silver halide or metal sulfide is used. Silver sulfide is an ion conducting material and exhibits larger silver ion conductivity than the corresponding halide compounds and can be easily pressed into thick disks. Because of its silver ion conductivity, this material shows a Nernstian response to silver ions in solution and is thus well suited for use in ion-selective electrodes. Such semi conductor like materials do not respond so strongly to redox systems because of their larger forbidden energy bands, which cannot accommodate any electrons. Sensitivity of iodide ion-selective electrodes is quite good and shows linearity in the range of 10^{-8} M to 1 M iodide. chloride and bromide do not interfere even if present at higher concentrations. Sulfide, cyanide and ammonia may interfere [14]. Strongly reducing solutions may damage the membrane by forming a layer of metallic silver on the surface. The surface then requires to be removed by polishing off. No interferences are caused by NO_3 , SO_4 , PO_4 , F, HCO_3 , nor by oxidizing agents such as Cu^{++} , Fe^{+++} or MnO_4^- . A linearity curve of iodide ion-selective electrode is shown in Fig. 2. The slope of the linear portion is 56.2 mV and linearity co-efficient of

variation r^2 is 0.99. Linearity of the curve is very good and value of the slope is also close to the expected slope of 60 mV. At very low concentrations the curve does not remain linear and one has to measure and calculate carefully the levels of iodide.

Coulometry is very sensitive and an absolute method, which can be used for the analysis of halides also. This method was used for intercomparison studies of halides with ion-selective electrodes. In Table 1 values of iodide measured in water samples by ion-selective electrode and coulometry are given, which are in agreement with each other.

Table 1. Comparison of iodide analysis by ion selective electrodes with coulometry

Sample	Coulometry (mg/L)	Ion-Selective Electrode (mg/L)
R ₁	0.21 ± 0.021	0.19 ± 0.018
R ₂	0.23 ± 0.022	0.20 ± 0.02
SI ₁	0.20 ± 0.016	0.23 ± 0.016
SI ₂	0.19 ± 0.02	0.21 ± 0.021

Table 2. Recoveries of added fluoride

Sample	Fluoride added ($\mu\text{g/L}$)	Measured Value ($\mu\text{g/L}$)	Recovery %
Sample-1	-	36.0	-
"	100	141.0	105
Sample-2	-	35.0	-
"	75	105.0	93

Reliability of the fluoride ion-selective electrode was checked by recoveries of the added standards to the samples. Recoveries of added fluoride were satisfactory (Table 2). Fluoride has very narrow permissible range. Permissible levels of fluoride as recommended by WHO are 1.5 mg/L [42] Water samples containing fluoride significantly less than 1mg/L may show deficiency problems and more than about 2 mg/L may cause toxicity problems. Thus monitoring of water samples for fluoride is very important.

After optimizing the ion-selective electrodes and measurement method, many water samples from different areas were measured for the contents of fluoride and iodide. Simly Dam and Rawal Dam are two main water reservoirs in Islamabad, which supply water to Islamabad and Rawalpindi respectively. Many water samples were collected from these reservoirs and analysed. In Table 3 average values of fluoride and iodide are given before and after water treatment from the water reservoirs. Slight increase in ion concentrations is observed after treatment.

Table 3. Levels of fluoride and iodide in Main Water Sources of Rawalpindi-Islamabad Before treatment.

Sample	Fluoride ($\mu\text{g/L}$)	Iodide ($\mu\text{g/L}$)
Rawal Dam	31.5 ± 2.8	192 ± 21
Simly Dam	34.0 ± 3.5	232 ± 26

After Treatment

	Fluoride ($\mu\text{g/L}$)	Iodide ($\mu\text{g/L}$)
Rawal Dam	$38.4 \pm 4.$	203 ± 30
Simly Dam	35.1 ± 3.2	210 ± 26

In Table 4 the values of fluoride and iodide in surface water samples randomly collected from different areas of Rawalpindi and Islamabad are given. Fluoride and iodide levels in these water samples are in the range of 15-152 $\mu\text{g/l}$ and 180 - 235 $\mu\text{g/l}$ respectively that are below the

Table 4. Levels of fluoride and iodide in surface water samples of Rawalpindi-Islamabad.

Sample	Place of Collection	Fluoride ($\mu\text{g/L}$)	Iodide ($\mu\text{g/L}$)
SW ₁	Simly Dam	34.1 ± 29	212 ± 25
SW ₂	Simly Dam	$36. \pm 3.0$	200 ± 21
SW ₃	Nilore (PINST.) IBD.	38.2 ± 3.1	233 ± 25
SW ₄	G-9/4, IBD.	15.6 ± 1.2	-
S ₁ W ₁	Rawal Dam, IBD.	35.0 ± 4	-
S ₁ W ₂	Rawal Dam M, Ibd	38.5 ± 3.6	180 ± 25
S ₁ W ₃	R. G. Hospital, RWP	93 ± 8	200 ± 21
S ₁ W ₄	B. Block, S. Town, RWP	152 ± 6	-
S ₁ W ₅	D. Block, S. Town, RWP	57 ± 6	-
S ₁ W ₆	Asghar Mall Rd, RWP	38 ± 4	211 ± 24
S ₁ W ₇	Saidpur Road, RWP	23 ± 3	-

permissible limits and small variations may be due to the any local contamination problems from the water distribution system and at the specific site. Three samples S₁W₃, S₁W₄ and S₁W₅ from Satellite town have some higher values of fluoride as compared to other samples. These three areas are in close vicinity and may have some source of fluoride addition. Amounts of iodide are nearly the same in all the samples.

Levels of fluoride and iodide in ground water samples collected from Rawalpindi and Islamabad area are given in Table 5. Variations in ground water samples are significant. Ranges of fluoride and iodide are 23-1300 $\mu\text{g/l}$ and 15-5710 $\mu\text{g/l}$ respectively. These significant variations in the levels of fluoride and iodide within a few kilometers area point out that the local effects are responsible depending upon the underground soil composition. Obviously there is a need for stringent quality control before distribution for consumption purposes and this is particularly true for fluoride. Levels of fluoride in samples GW₂, GW₄ and G₁W₉ are very high. In these areas ground water is mostly used for drinking purposes. Samples G₁W₄, G₁W₅ and G₁W₁₁ have also medium to higher concentrations of fluoride. In rest of the samples the levels of fluoride are nearly comparable to surface water samples. In Table 6 are given the values of fluoride in ground water samples provided to our lab. For analysis from a village near Lahore where numerous bone softening and

Table 5. Levels of Fluoride and Iodide in ground water samples of Rawalpindi-Islamabad.

Sample	Place of Collection	Fluoride ($\mu\text{g/L}$)	Iodide ($\mu\text{g/L}$)
GW ₁	Chirah, IBD	34.0 $\pm$ 2.2	386 $\pm$ 26
GW ₂	Alipur Farash, IBD	759 $\pm$ 40	2280 $\pm$ 159
GW ₃	Tumair, IBD	95 $\pm$ 7	190 $\pm$ 18
GW ₄	Shakrial, RWP	1300 $\pm$ 97	-
G ₁ W ₁	Amarpura, RWP	44 $\pm$ 5	-
G ₁ W ₂	Waris Khan, RWP	7 $\pm$ 6.2	-
G ₁ W ₃	Fazalabad, RWP	23.6 $\pm$ 2.6	-
G ₁ W ₄	Sultanpura, RWP	285 $\pm$ 22	5710 $\pm$ 15
G ₁ W ₅	Talian Shahan RWP	265 $\pm$ 26	250 $\pm$ 17
G ₁ W ₆	Fazalabad RWP	26.0 $\pm$ 3	-
G ₁ W ₇	Faizabad, RWP	93 $\pm$ 8	-
G ₁ W ₈	Faiz-ul-Islam, High School,	23.5 $\pm$ 2.6	-
G ₁ W ₉	Chaklala, RWP	1280 $\pm$ 112	57 $\pm$ 6
G ₁ W ₁₀	Churh Harpal, RWP	76 $\pm$ 8	15 $\pm$ 2
G ₁ W ₁₁	Sultan pura, RWP	361 $\pm$ 45	114 $\pm$ 9

Table 6. Levels of fluoride from Lahore area

Sample	Fluoride ($\mu\text{g/L}$)
LB-8	7980 $\pm$ 695
LR-9	8935 $\pm$ 760
LR-10	3336 $\pm$ 275
LB-11	1105 $\pm$ 125
LB-12	210 $\pm$ 18
LB-13	185 $\pm$ 21
LB-14	8625 $\pm$ 955
LR-15	20250 $\pm$ 1895
LR-16	4108 $\pm$ 510
LR-10	120 $\pm$ 15

bone deformation cases particularly in children were reported. Levels of fluoride in these samples are very high which have caused health hazards for human beings. Toxic effects of fluoride increase significantly for children with poor diet and health. It may cause softening of bones causing permanent disability, and thus endangering the lives of poor segments of the society. Purpose of giving Table 6

is not to find any co-relations but to further stress of conclusion of Table 4 that levels of fluoride in ground water samples can vary significantly even in the same area from different wells. In addition to soil composition underground water may also be contaminated from industrial waste because fluoride is extensively used in many industries particularly cable and wire and rubber industries.

The levels of fluoride in four water sources i.e. Rawal Dam, Simly Dam, Swat River and Kabul River are compared in Table 7. Swat and Kabul rivers are in the northern hilly regions of Pakistan where these are a source of drinking water. Levels of fluoride and iodide are lower in surface water sources of northern areas.

The daily intake of fluoride and iodide by human beings using water from different water sources are calculated. Daily intakes are calculated assuming consumption of water is 3 liters per person per day. Daily intake of fluoride and iodide in northern areas is significantly lower than even from Rawalpindi and Islamabad area, which points out that there may be deficiency problems of iodide and fluoride among population, which may cause goiter and caries. It may be concluded that levels of iodide are generally low in all water samples and

Table 7. Comparison of fluoride and iodide in water from different areas of Pakistan

Place of Collection	Fluoride ($\mu\text{g/L}$)	Fluoride intake ($\mu\text{g/L}$)	Iodide ($\mu\text{g/L}$)	Iodide Intake ($\mu\text{g/L}$)
Rawal Dam	35 ± 3	105	190 ± 20	570
Simly Dam	34 ± 4	102	230 ± 22	690
River Swat	2	6	33 ± 5	99
Kabul River	2	6	15 ± 2	45

are very low in northern hilly regions and there is a need to take additional iodine and it is particularly necessary in northern areas. Levels of fluoride in surface water samples are low and surface water is safe for drinking purposes regarding fluoride. Ground water needs to be strictly controlled for the levels of fluoride. Some areas in northern regions may also have higher levels of fluoride in ground water but in southern regions many areas need to be closely monitored for levels of fluoride in the ground water and it is particularly true for industrial areas to avoid fluorosis.

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