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Comparison of Fluoride Ion-Selective Electrode Based Potentiometric Methods of Fluoride Determination in Human Urine

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Small amounts of fluorine are vital for the human body; although larger quantities of it are toxic. The most characteristic symptoms of a small overdose of fluorine are nausea, vomiting, salivation, stomach-ache and diarrhoea (Clark 1981; Drozdz 1984). With larger doses convulsions, heart arrhythmia and coma (sleeping sickness) are common. The difference between fluorine need and a harmful dose for humans is very small. The lethal dose for adults is 0.20-0.35 g F^- per kg body weight. A dose of above *ca.* 20 mg (for some people even less) causes severe toxic effects (Jedrzejczuk and Milewski 1996). Therefore fluoride content in humans should be accurately monitored. Urine, which is the main path of fluoride excretion from the human body, should be selected for monitoring.

Electroanalytical methods based on potentiometry with ion-selective electrodes seem to be the most popular and convenient methods of fluoride ion determination (Wen et al. 1996; Wen et al. 1998). Aqueous matrices are generally the easiest to analyse, since generally sample preparation is simple, or not required at ail. Typical applications include the determination of fluoride ion in drinking water (Ortiz et al. 1998) rain water (Hara and Huang 1997) aqueous solution (Papaefstathiou et al. 1995) serum (Torra et al. 1998) etc. The accuracy of the analysis depends, to some extent, on the calibration procedure (direct reading potentiometry, single or double standard addition, bracketing solutions, Gran's method) (Cammann, 1977).

The aim of this work is to compare those quantitative potentiometric methods of fluoride determination in urine which are based on the application of the fluoride ion-selective electrode.

MATERIALS AND METHODS

Fluoride ion was determined potentiometrically with the use of a F-804 Detektor fluoride ion-selective electrode (Detektor S.C. Aparatura elektrochemiczna, Warsaw, Poland) and an Elmetron pH-meter, model Cl-316 (Elmetron S.C., Zabrze, Poland) operated in the

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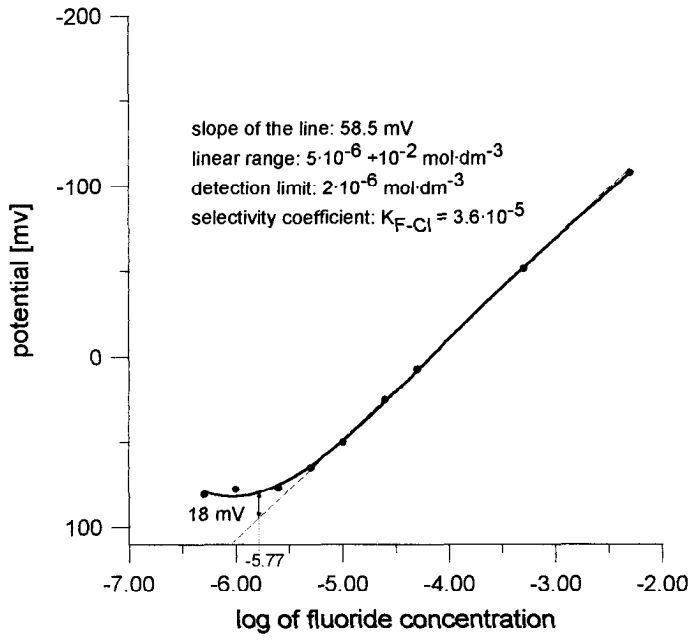


Figure 1. Characteristics of the F-804 fluoride selective electrode.

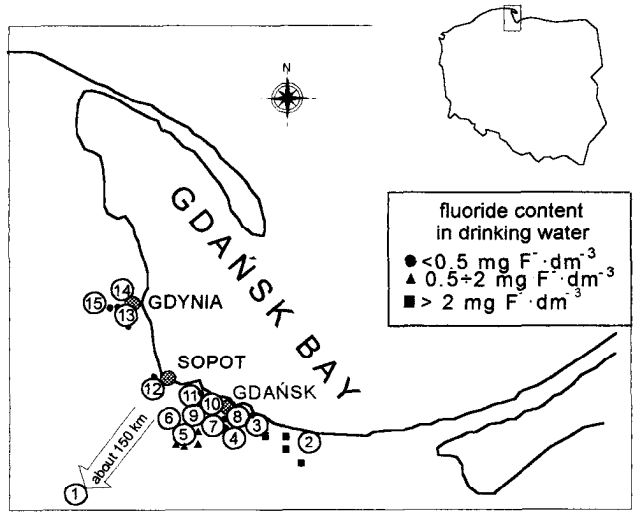


Figure 2. Location of the studied populations.
1- Lipka Krajeńska; 2- Sobieszewo; 3- Gdańsk Przeróbka; 4- Gdańsk; 5,6- Gdańsk Wrzeszcz; 7- Gdańsk Zaspa;8- Gdańsk Nowy Port; 9-Gdańsk Oliwa, 10- Gdańsk Brzeźno; 11- Gdańsk Przymorze; 12- Sopot; 13- Gdynia Witomino; 14- Gdynia; 15- Gdynia Pogórze.

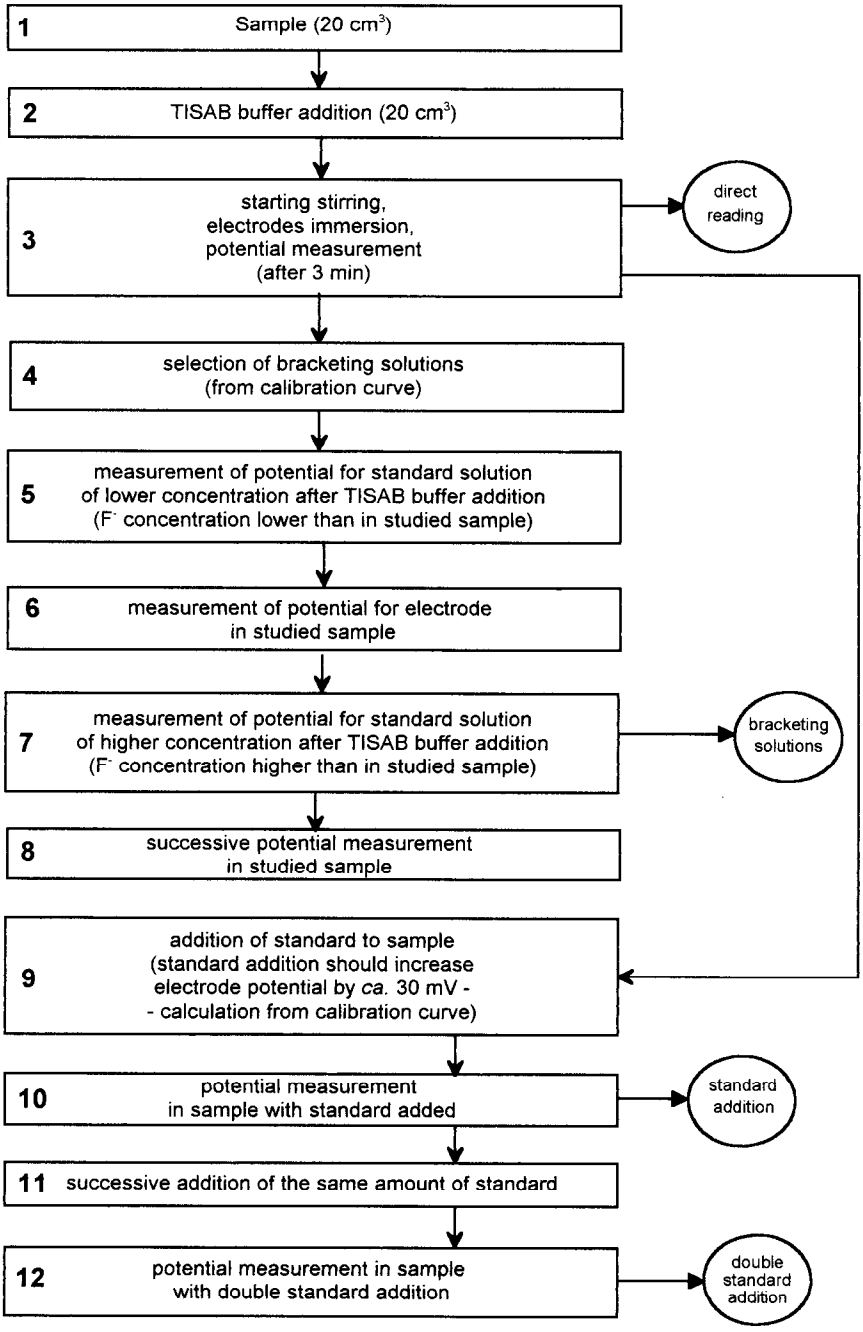


Figure 3. Schematic diagram of a fluoride concentration measurement method by means of potentiometric techniques.

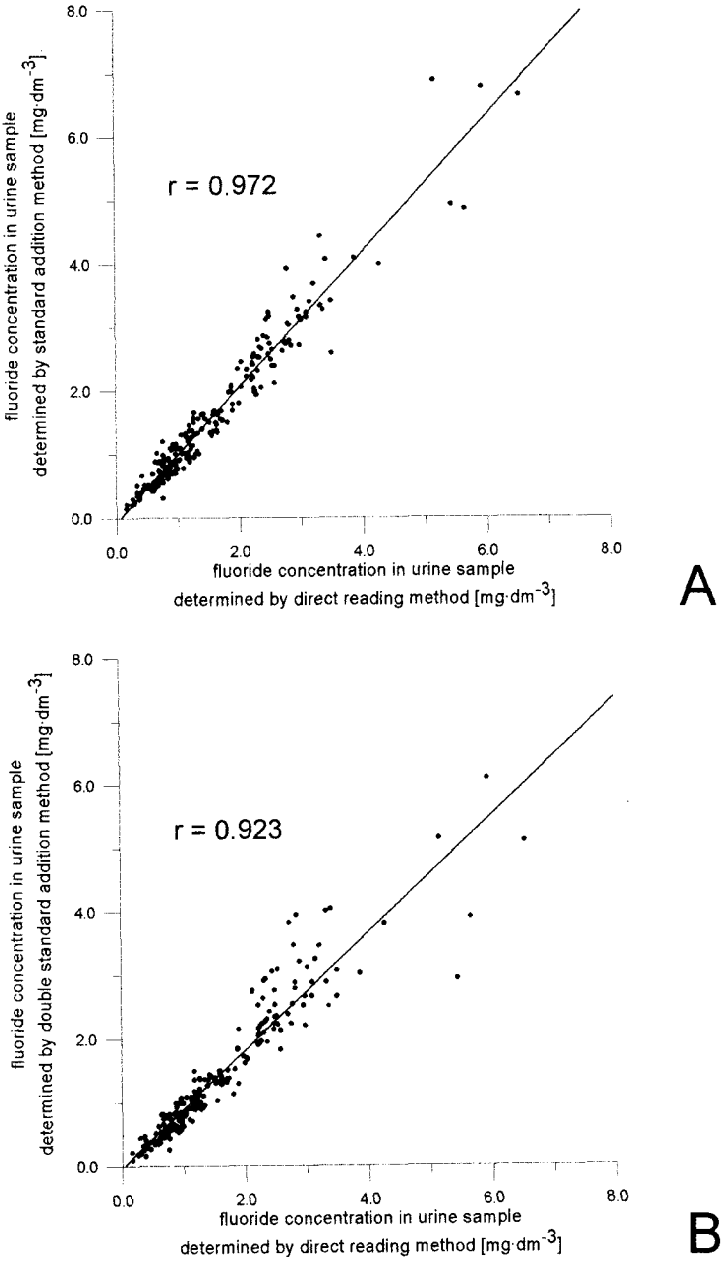
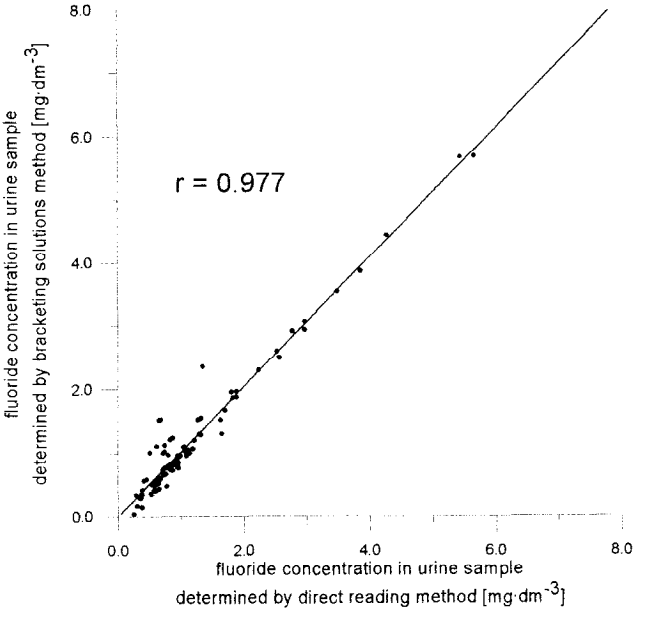
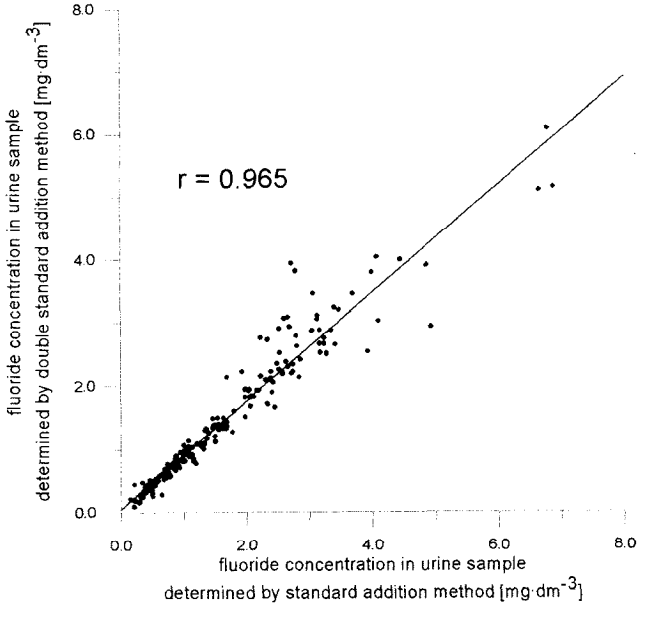


Figure 4. Correlation between the results of fluoride determination in urine with different quantitative methods:
A - direct reading *vs.* standard addition;
B - direct reading *vs.* double standard addition;



C

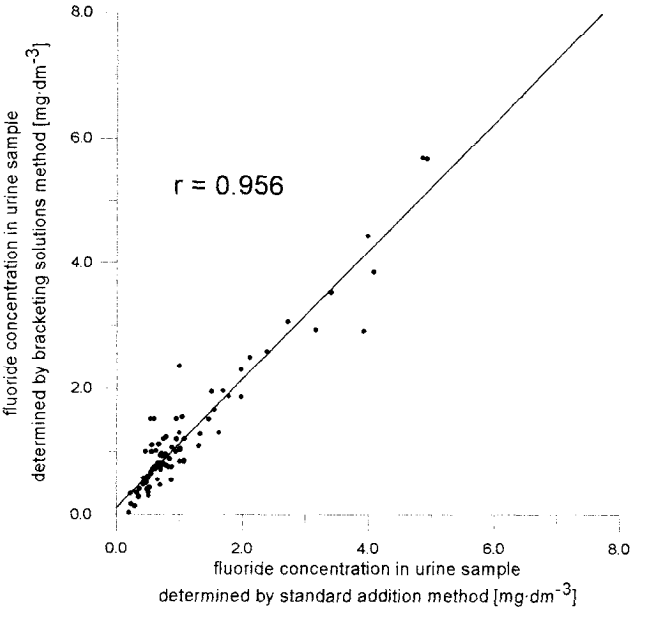


D

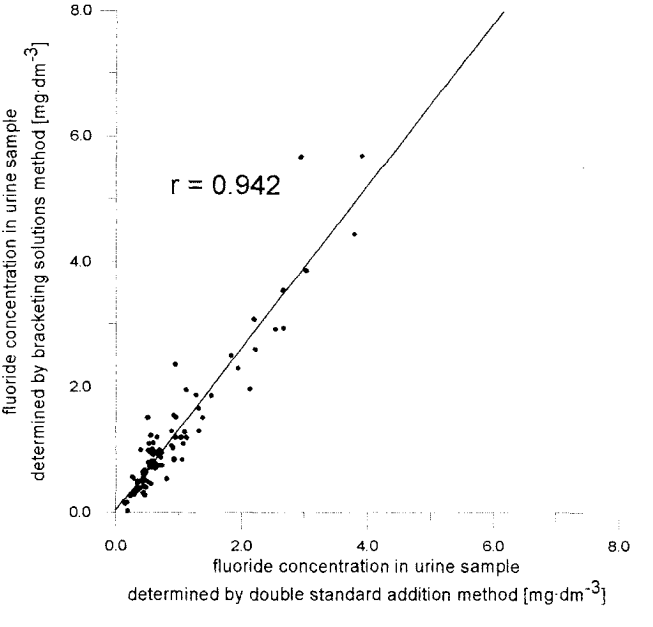
Figure 4. *continued*

C - direct reading vs. bracketing solutions;

D - standard addition vs. double standard addition;



E



F

Figure 4. *continued*

E - standard addition vs. bracketing solutions;

F - double standard addition vs. bracketing solutions.

Table 1. Statistical evaluation of the results obtained by different FISE based potentiometric methods.

	direct reading (DR)	standard addition (SA)	double standard addition (DSA)	bracketing solutions (BS)
number of results	**226**	**226**	**226**	**96**
direct reading - (DR)		f: SA=1.065·DR-0.061 a = -0.061 S_a = 0.033 b = 1.065 S_b = 0.035 r_{cal} = 0.972 $r_{crit}(0.05, 224)$ = 0.20 t^a_{cal} = 1.85 $t_{crit}(0.05, 225)$ = 1.97 t^b_{cal} = 1.86 $t_{crit}(0.05, 225)$ = 1.97	f: DSA=0.923·DR-0.030 a = -0.030 S_a = 0.035 b = 0.923 S_b = 0.019 r_{cal} = 0.946 $r_{crit}(0.05, 224)$ = 0.20 t^a_{cal} = 0.86 $t_{crit}(0.05, 225)$ = 1.97 t^b_{cal} = 4.05 $t_{crit}(0.05, 225)$ = 1.97	f: BS=1.023·DR-0.0065 a = -0.0065 S_a = 0.035 b = 1.023 S_b = 0.023 r_{cal} = 0.977 $r_{crit}(0.05, 94)$ = 0.21 t^a_{cal} = 0.19 $t_{crit}(0.05, 95)$ = 1.98 t^b_{cal} = 1.00 $t_{crit}(0.05, 95)$ = 1.98
standard addition - (SA)			f: DSA=0.859·SA+0.044 a = 0.044 S_a = 0.027 b = 0.859 S_b = 0.014 r_{cal} = 0.965 $r_{crit}(0.05, 224)$ = 0.20 t^a_{cal} = 1.63 $t_{crit}(0.05, 225)$ = 1.97 t^b_{cal} = 10.1 $t_{crit}(0.05, 225)$ = 1.97	f: BS=1.022·SA+0.011 a = 0.011 S_a = 0.047 b = 1.022 S_b = 0.033 r_{cal} = 0.956 $r_{crit}(0.05, 94)$ = 0.21 t^a_{cal} = 0.23 $t_{crit}(0.05, 95)$ = 1.98 t^b_{cal} = 0.67 $t_{crit}(0.05, 95)$ = 1.98
double standard addition – (DSA)				f: BS=1.294·DSA+0.033 a = 0.033 S_a = 0.056 b = 1.294 S_b = 0.048 r_{cal} = 0.942 $r_{crit}(0.05, 94)$ = 0.21 t^a_{cal} = 0.59 $t_{crit}(0.05, 95)$ = 1.98 t^b_{cal} = 6.10 $t_{crit}(0.05, 95)$ = 1.98

where:

f - linear regression function;
a - intercept;
b - slope;
r_{cal} - calculated value of regression coefficient;
t^a_{cal} - calculated value of *t-Student* parameter ($t^a_{cal} = a/S_a$)
t^b_{cal} - calculated value of *t-Student* parameter ($t^b_{cal} = (1-b)/S_b$)

S_a - standard deviation of intercept,
S_b - standard deviation of slope;
r_{crit} - critical value of regression coefficient for (α, ν);
t_{crit} - critical value of *t-Student* parameter for (α, ν);
t_{crit} - critical value of *t-Student* parameter for (α, ν);
α - significance level;
ν - degrees of freedom;

millivoltmeter mode (with an accuracy of 0.1 mV). A silver chloride reference electrode (DRJ 710 Detektor) was also manufactured by Detektor S.C.. The determination of fluoride in the urine was preceded by measuring the characteristics of the F^- 804 Detektor indicator electrode and selecting the optimum calibration method (used as a reference method).The characteristics of the electrode are given in Figure 1.

To minimise the matrix effect, a total ionic strength adjustment buffer (TISAB) from Merck, Germany was used. This buffer (pH 5-6) contains sodium chloride (>58 g/L) and trans-1,2-diaminocyclohexane-N,N,N',N'-tetraacetic acid (>3.6 g/L). Working standard fluoride solutions were prepared by diluting commercial standard F^- solution of 1000 F^- mg/L concentration (Merck, Germany) with deionized water.

Urine samples were collected from children attending kindergartens in selected districts of the Tricity (Gdansk, Gdynia, Sopot). The children from a given kindergarten generally lived within its vicinity. The location of the populations studied and the corresponding concentrations of fluoride in drinking water (Geschwind and Jurkiewicz 1952) are depicted in Figure 2.

For sampling, typical polypropylene containers used for medical analysis were distributed among the children's parents. The urine samples were collected in the morning and delivered to the analytical laboratory on the same day. The samples were stored at 4 °C. They were usually analysed on the day of delivery.

Fluoride was quantified using direct reading potentiometry, single and double standard addition methods (Cammann 1977) and a method of bracketing solutions. In the single standard addition, the standard F^- solution was added to the samples in such amounts so as to change an electrochemical cell potential by about 30 mV. In the bracketing solution method two standard fluoride solutions were used: one of a fluoride concentration lower and the second of a fluoride concentration higher than that in the sample studied. To use this approach, the approximate concentration of fluoride ion in the sample was first measured by means of the direct reading method. To minimise analytical errors the working standard fluoride solutions used as bracketing solutions were prepared to differ as little as possible from the fluoride concentration in the real sample. The schematic diagram of the analysis is presented in Figure 3.

RESULTS AND DISCUSSION

Monocrystalline fluoride electrode based potentiometry can be used to determine fluoride concentration in drinking water as well as in urine due to its high sensitivity, specificity (low response to interfering ions), wide linear range (over 4 decades) and low detection limits ($2 \cdot 10^{-6}$ mol $F^- \cdot dm^{-3}$). The advantages of this approach include: a short analysis time (less than 5

min), elimination of sample pretreatment in the majority of cases, easy reduction of possible matrix effects (TISAB addition), simplicity of the measuring system and relatively low instrument costs.

The concentration of fluoride ion was determined in 226 urine samples. All the samples were analysed with use of the direct reading and single and double standard addition methods. The bracketing solutions method was used for 96 real samples only.

The results of fluoride determination in urine given by the quantitative analytical methods (direct reading, standard addition, double standard addition, bracketing solutions) were paired, and for each pair one was plotted as a function of the other (Figure 4), showing the comparative accuracy. In all cases, the correlation was good (linear regression coefficients were higher than 0.94).

For the plots of direct reading vs. bracketing solutions, direct reading vs. standard addition and standard addition vs. bracketing solutions, slopes were not significantly far from 1 and intercepts were not significantly far from 0, at the significance level of 0.05 (Table 1). This indicates that these three methods did not differ in accuracy, at the significance level of 0.05. It is therefore highly probable that they gave accurate results. This is not the case with the double standard addition method, which gave fluoride concentration statistically significantly lower than that obtained by any of the three other methods.

Monocrystalline fluoride electrode potentiometry with either a direct reading or standard addition or bracketing solutions method of calibration is appropriate to determine low content of fluoride ion in drinking water and urine.

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