MEASUREMENT OF FLUORIDE IN MAGADI

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SUMMARY: The concentration of fluoride is measured in a crystalline magadi sample, originating from Lake Magadi, after it has been pre-treated in three different ways. The results show that the measured fluoride concentration is independent of the amount of magadi dissolved in water, though high concentrations, like 30 g magadi/l, results in high ionic strength of the solution, which may interfere in the fluoride analysis. A big lump is crushed into small pieces and these are analysed for fluoride. The concentrations measured are subject to wide variation and there are significant differences in the concentrations. The concentration seems to follow a logarithmic distribution. Crushing and sieving before analysing, results in significant differences in the measured concentrations. Grains smaller than 1.0 mm have a significant higher concentration than grains bigger than 1.0 mm. Additionally crushing of grains bigger than 4.0 mm does not result in variation in the concentration.

Key words: Magadi; trona; fluoride concentration; sieving; dilution.

INTRODUCTION

The special geological and hydrological conditions at the East African Rift Valley cause both ground water and surface water in big parts of Kenya and Tanzania to be alkaline and contaminated with fluoride (low Ca^{2+}, high Na^{+}, CO_3^{2-} and F^{-}). As a result, salt deposits are formed at the alkaline lakes and on the earth's surface due to evaporation. The salt deposits consist mainly of trona ($Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$) contaminated with fluoride. This is locally called magadi.

In trona, fluoride is occurring as villiaumite (sodium fluoride) and it has been observed[1] that well-formed cubic crystals of villiaumite is occurring as inclusions in the larger trona crystals and it also occurs as clots of crystals adhering to the margins of the trona crystals. The fluoride concentration in magadi varies a lot, 0.2-14.9 mg F^{-} /g magadi[1-4] not only depending on the origin.

This paper evaluates three different pre-treatments before measurement of fluoride concentration in magadi solutions and the influence of the pre-treatment on the measured value.

MATERIALS AND METHODS

Magadi Samples: The magadi samples used in the investigation is from Lake Magadi, Kenya and was bought at the market in Magadi town November 1993. The sample is crystalline and grey in colour. The crystals have form like needles to a length of 30 mm.

Crushing and Sieving: The magadi sample is crushed in a mortar and dissolved in distilled water. Thereafter the fluoride concentration is measured.

Fluoride measurements: The fluoride concentration is measured using a Radiometer F1052 fluoride electrode and a Metrohm Ag/AgCl reference electrode with a sleeve type diaphragm connected to a Metrohm potentiometer (692 pH/Ion Meter). A 10-ml sample of the solution is mixed with 10 ml CDTA-tisab and the fluoride

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concentration is measured using the calibration method according to Standard Mehods[5]. If the reading on the potentiometer is higher than a concentration equal to 10 mg/l the sample is diluted additionally.

Preparation of solutions: The magadi is treated in three different ways before it is dissolved in distilled water. In the first investigation a big lump (40 g) is crushed into powder. Different dilutions, 5.0, 10, 20, and 30 g magadi/l, are prepared (4-5 replicates) and analysed for fluoride. In the second part a big lump (500 g) is crushed into 20 smaller parts. These small samples are crushed into powder and dilutions of 20 g/l are prepared (2 replicates) and analysed for fluoride. In the last investigation a lump of 150 g is crushed into small particles and sieved in a electrical shaker for 5 minutes using the sieve sizes: 0.50, 0.71, 1.0, 1.4, 2.0, and 4.0 mm. Dilutions of 20 g/l are prepared (3 replicates) for each grain size fraction and analysed for fluoride.

RESULTS AND DISCUSSION

Magadi Solutions: The results from the experiment with different magadi dilutions can be seen in Table 1. The ionic strength of the solution, I, is calculated according to the Debye-Hückel theory[9], $I=\frac{1}{2}\sum m_i \cdot z_i^2$, assuming that the magadi sample is pure sodium sesquicarbonate ($Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$).

It is seen that the measured fluoride concentration varies for different amount of dissolved magadi in distilled water. A single factor ANOVA (ANalysis Of VAriance) shows that there is no significant difference between the fluoride concentrations in the different dilutions. No relation between the ionic strength and the fluoride concentration can be found either.

TABLE 1: The fluoride concentration in a magadi sample and the ionic strength (I) of the solution according to the Debye-Hückel theory[6].

Dilution g-magadi/L	No of Samples	Con. mg-F/g-magadi	I mol/L
5.0	5	0.291	0.088
10	5	0.280	0.177
20	5	0.265	0.354
30	4	0.285	0.531

The ionic strength of the solution has to be taken into consideration though. The CDTA-tisab is mixed with the dilution to keep a constant ionic strength, resulting in a hardly varying activity coefficient. The addition of CDTA-tisab to a water sample with low ionic strength (for example drinking water) results in a ionic background strength of 2.0 mol/l[7] and addition of 30 g sodium sesquicarbonate to 1 litre of distilled water results in a ionic strength of 0.53 mol/l. Therefore different amounts of dissolved magadi result in varying ionic strength and therefore higher uncertainties in determination of the fluoride concentration. Thus, small amounts of magadi have to be dissolved in distilled water before measurement of fluoride concentration when using the calibration method.

Distribution Differences: The fluoride concentration (average of 2 replicates) in the 20 small samples can be seen in Figure 1. The cumulative frequency is plotted versus the fluoride concentration on logarithmic probability paper. It is obvious that the fluoride concentration is subject to a wide variation and a single factor ANOVA shows significant differences between the measured fluoride concentrations in the small samples. The concentration ranges from 0.09 to 0.20 mg-F/g-magadi and the fractiles of 25, 50, and 75% being 0.102, 0.115, and 0.137 mg/g. From the plot in

Figure 1 it is seen that the fluoride concentration in the magadi sample seems to follow a logarithmic distribution.

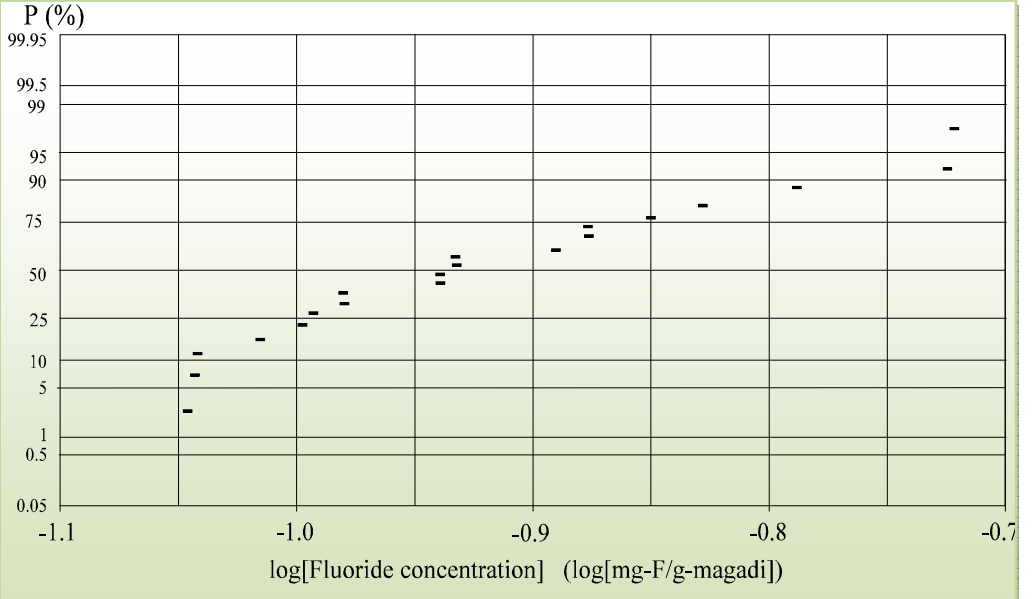

FIGURE 1. The fluoride concentration in 20 small samples from the same lump plotted on logarithmic probability paper.

Grain sizes: The results from the sieving investigation can be seen in Figure 2. The measured fluoride concentrations (3 replicates) are plotted versus the geometric mean grain size, GS_{gm}.

From Figure 2 an obvious dependency between the grain size and the fluoride concentration is observed, that is the fluoride concentration is decreasing for increasing grain sizes. It seems as the concentration stabilises at a certain level for GS_{gm} higher than 1.18 mm. A single factor ANOVA shows a significant difference between the grain sizes and a Newman-Keuls Range Test shows that the concentration for GS_{gm}, equal to 0.22, 0.59, and 0.8 mm are significantly higher than the concentration for the other grain sizes. All grains bigger than 1.0 mm (GS_{gm}=1.18) has the same

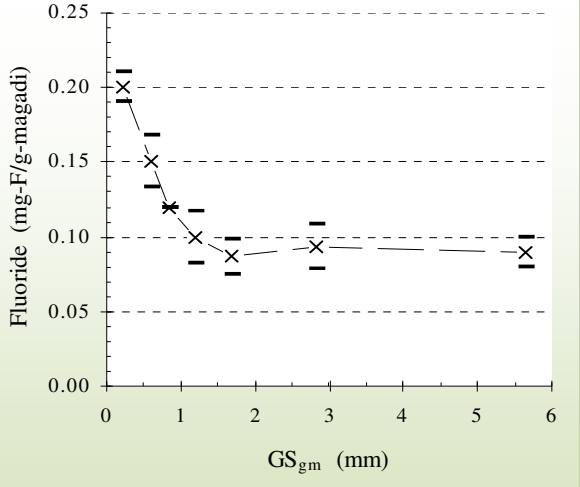

FIGURE 2. The fluoride concentration (3 replicates) versus the geometric mean grain size, GSgm. x indicates the mean, and - indicates the standard deviation.

fluoride concentration, approximately 0.09 mg F^-/g magadi.

For further investigations of the relationship between the fluoride content and the grain size, grains bigger than 4.0 mm (GS_{gm} = 5.66 mm) are additionally crushed and sieved using the mesh sizes 0.125, 0.18, 0.25, 0.50, 0.71, 1.0, and 1.4 mm. Dilutions of 20 g/l are prepared (single measurement) for each grain size fraction and analysed for fluoride. The result of a single measurement can be seen in Figure 3.

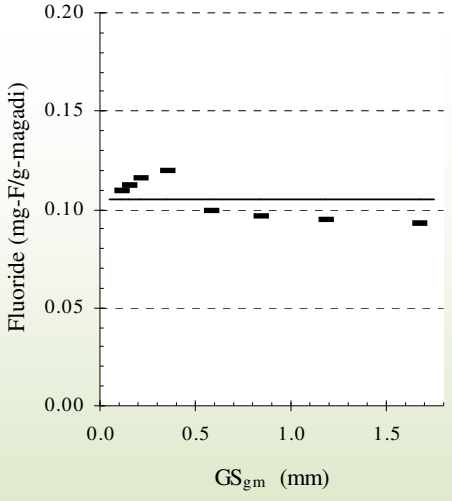

FIGURE 3 Single measurement of the fluoride concentration in a magadi sample (d>4.0mm) versus the geometric mean grain size, GS_{gm}, after additional crushing and sieving. - indicates the measurements and the straight line indicates the average.

It is observed that the fluoride concentration is stable, 0.105 mg-F^-/g-magadi for all grains after additional crushing and sieving of grains bigger than 4.0 mm. This is not in agreement with Baker[1] who found that fluoride was mainly present in the +4mm and -60 mesh B.B.S. (≈0.50 mm) fractions of crushed magadi. Baker[1] also found that when crushing the coarser fraction fluoride passed into the fine products.

From the above given results it is recommended that a big sample is crushed into powder and mixed well before analysing for fluoride. If only a small amount of magadi is available it should be kept in mind that the measured fluoride concentration is not a very good estimate of the true fluoride concentration.

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