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DETERMINATION OF TRACE METAL CONTENT OF GÖKCEADA CURING MUD BATH BY AAS

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Abstract- Trace metal ion concentrations of the mud bath of the Gökceada region were investigated to determine Cr, Pb, Bi, Ni, Cu, Fe, Mn, Zn, Cd, Ca, Mg, Ba and As content by AAS. The concentrations of Cr and Cd were found below the detection limit of flame AAS so they could not be determined. Mg and Ca were higher in concentrations, as expected, and Co, Cu and Ni were the lowest detectable quantities in the samples measured by Flame AAS.

Keywords: determination, trace metal, slurry, Gökceada, mud bath, Atomic Absorbtion Spectrophotometry (AAS).

1. *INTRODUCTION*

Gökceada is an island located in the Agean Sea near the north-west corner of Anatolia. It is 32 km away from Canakkale (Dardanel) and 18 km away from Gelibolu. It has a surface area of 289 km^2 and a population of 8500 in 1990. It is famous for its curing mud bath which originated from its salt lake and a well-known touristical holiday village. The lake is 200 m away from the coast and is at sea level. The composition of the lake water is not clear, but muddy.

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The lake surface is covered with a crystalline salt layer which is removed before the application of the mud to the skin for curing dermatological diseases and skin care. Since the chemical composition of the mud was not examined before, it would be interesting to determine the metal content of the mud used widely by the people visiting the island. In this work, the metal concentrations of the slurry were determined by AAS technique and the results were discussed from an analytical and an environmental point of view. The presence of some essential and useful elements for the human body in the mud encouraged us to publish the results for future detailed investigation of the mud.

2 *EXPERIMENTAL*

2.1 Sampling

All the mud samples were collected from different regions of the lake from 15-20 cm depth after removing the salty layer of the surface as is done by the people who use the mud. The six samples of different regions were mixed and kept sealed in a bottle at room temperature until the analysis performed. The sample is brownish-black in color and has very fine particles sized smaller than that of ordinary sea sand. The mixture was divided into three parts, each of which was prepared and analized separately.

2.2 Preparation to the analysis:

From each mud sample approximately 15 g were taken and dried in an oven at 110°C and the water content of the each sample was measured. From each of three dried samples, ~2 g were weighed and dissolved in Aqua Regia by heating under reflux condenser to have a organic free and an easily soluble sample. The heating procees was repeated three times until drieness in each time [3]. 50 ml of 2M HNO_3 was added to the dried samples and the mixture

was heated until a clear solution obtained. The samples were filtered through Gouche crucible and the unsoluble fraction of silicates was determined. The clear solution was used for an AAS measurement after dilution to 100 ml [3].

2.3 Measuring Condition

All the samples were analyzed by Perkin Elmer Model 3110 Flame Atomic Absorption spectrophotometer. Atomization was performed by Asetilene / Air flame with a flow rate of 2.5 l/h for Asetilene and 6 l/h for air.Two types of sources from Cathedon and Perkin-Elmer were employed to excite the elements. The slit width was adjusted to either 0.2 nm or 0.7 nm. The current applied for each element varied from 6-30 mA depending on the element.

2.4 Preparation of Standard Solutions

All the standard solutions were prepared from analytical grade compounds of Merck Company. The following salts of the metals were employed for the preparation of the standards: $ZnCl_2$, $CdCl_2 \cdot H_2O$, $Bi(NO_3)_3 \cdot 5H_2O$, $Pb(NO_3)_2$, $Fe(NO_3)_3 \cdot 9H_2O$, $MnSO_4 \cdot H_2O$, $Co(NO_3)_2 \cdot 6H_2O$, $MgCl_2$, As_2O_3, $Cr(NO_3)_3$, $CuCl_2 \cdot 2H_2O$, $Ni(NO_3)2 \cdot 6H_2O$, $Ba(NO_3)_2 \cdot H_2O$, $Ca(NO_3)_2$. For each element, six standard solutions of different concentrations in the linear range were prepared in 2M of HNO_3, the optimum linear concentration range for the measurement [4]. The calibration curves were prepared for each of the elements investigated. The least square fitting was employed to get the best line in the linear range of the calibration lines. The equation of the best calibration line for each element can be seen in Table 1.

3 RESULTS AND DISCUSSIONS

The average density of the mud samples was found to be 1.516 ± 0.001 g/ml. The average water content of the mud samples was 50.4% (w/w) and the insoluble silicate content of the dried samples was found to be 37.59 % (w/w).

Table 1. The concentrations of the elements and their calibration curves

Element	Linear Range, µg/ml	Equations of calibration curves	Concentration ± σ (µg/g dried sample)
Cr	5.0 - 50.0	y = 1.1110 x + 0.0456	Below DL
Pb	2.0 - 20.0	y = 4.2154 x + 0.3346	361 ± 28
Bi	5.0 - 50.0	y = 0.9329 x + 0.4143	108 ± 6.5
Co	1.0 - 10.0	y = 22.5263 x - 2.8421	18.36 ± 0.13
Ni	2.0 - 12.0	y = 4.3500 x - 0.5571	39.7 ± 1.6
Cu	1.0 - 10.0	y = 15.6399 x + 0.3089	32.4 ± 3.9
Fe	1.0 - 10.0	y = 22.5602 x - 0.7153	9591 ± 410
Mn	0.5 - 5.0	y = 9.0278 x - 0.0455	1272 ± 140
Zn	0.2 - 2.0	y = 82.6433 x + 2.2730	648 ± 18
Cd	0.2 - 2.0	y = 53.3703 x + 0.8720	Below DL
Ca	5.0 - 50.0	y = 19.2502 x + 0.0033	22147 ± 36
Mg	10.0 - 60.0	y = 2.8821 x + 2.8221	34261 ± 13
Ba	20.0 - 150.0	y = 0.0742 x - 0.2844	3112 ± 84
As	40.0 - 150.0	y = 0.5420 x - 1.4873	2566 ± 43

DL: Detection Limit

The average pH of the mud was measured as 7.74 after dilution with water in a ratio of 1/1. The measured concentrations of each metal as µg/g(dry sample) were listed on Table 1. The linear range for the measurements of each metal and the equation of the calibration lines of each element are also given in the same table. It can be seen from the table that most of the elements show nearly the same linear range in that the upper concentration limit is ten times

higher than the lower concentration limit, excluding the ranges for Ni, Mg, Ba and As as they have narrower ranges. Among these three, As has the narrowest range with 40.0-150.0 μg/ml. The measured concentrations of the elements can be listed in a decreasing order as; Mg, Ca, Fe, Ba, As, Mn, Zn, Pb, Bi, Ni, Cu, Co, (Cr and Cd). The standard deviations of the concentrations measured for the elements were shown in the last column as ± σ.

The useful functions and the toxic effects of these elements were outlined in many publications[5,6,7,8,9,10] but the discussion of the health effects of these elements will be the subject of another study which will be performed by a medical and biomedical group in the university.

In most of the publications referenced above, it was reported that the following 18 elements are **essential** for the human body: **C, N, O, P, S, Cl, I, H, Na, Mg, K, Ca, Mn, Fe, Co, Cu, Zn, Mo**.

Additionally, a group of elements is said to be **useful** that one can live without that element but its absence causes health problems. **Si, F, Br, Sn, Ni, V, Cr, Se** are in this group.

Some elements are known as **unnecessary** or **contaminating** elements. They are present in each tissue, their concentrations vary and their physiological effects are not known.

All these elements have a spectrum of biological effects depending on the location of presence, concentration and the type of chemical compound formed. Therefore it is not easy to say something about the mechanism of the healing or useful effects of this curing mud on specific diseases, but the presence of some essential elements like Mg, Ca, Fe, Co, Cu, Zn, Mn, and the presence of useful elements like Ni, Cr in the mud can be helpful for some dermatological health problems, but discussion of this topic will not go further here.

REFERENCES

1. Parla,I. (Ed.), **Yurt Ansiklopedisi**, Anadolu Yayıncılık A.Ş., V.3, pp.1875, İstanbul, 1984

2. Demir,M., **Dissertation**, İnönü Üniversitesi, Malatya, 1986

3. Allen,S.E., Chimshow,H.M., **Chemical Analysis of Ecological Materyals**, John Willey, New York, 1974

4. Black,C.A., **Methods of Soil Analysis**, Prentice-Hall, Englewood Cliffs, 1965

5. Ozalp,M.N., Uzunismail,H., Bingöl,F., **SSK Gen.Müd.Yay.** No: 322, Ankara, 1978

6. Ozalp,M.N., Bingöl,F., Öğüş,A., **SSK Gen.Müd.Yay.** No: 334, Ankara, 1978

7. Avşarlıoğlu,M., **Türkiye Kaplıcaları ve İçmeleri Klavuzu**, Ankara, 1968

8. İstanbul Üniversitesi Tıp Fakültesi Hidro Klimatoloji Kürsüsü Üyeleri, **Türkiye Maden Suları-I**, İstanbul, 1970

9. Fiabane,D.R., Williams, A.M., **The Principles of Bio-inorganic Chemistry**, Chemical Society Monogram Series, London, 1977

10. Dogan M., **Eser Elementlerin Biyolojik Önemi**, Ders Notu, 1995

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