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FT-IR, EDXRF Analysis of the Mardin-Mazidag Phosphate Deposit of Turkey and Relations between Phosphate, Uranium and Fluorine

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EDXRF and FT-IR spectral analyses of the composite sample of Mardin-Mazidag phosphate deposit, in which the main phosphate mineral has been known to be collophane and dahllite, were reported. Uranium, phosphate and fluorine contents of the 25 individual phosphate samples were analyzed by EDXRF (U and P) and wet chemical methods (F). Quadratic regression model were applied on the U, P and F analyses results, in order to show the interrelation between phosphate, uranium and fluorine contents.

Key Words: Collophane, Dahllite, EDXRF, FTIR, Phosphate minerals, Quadratic regression analysis.

INTRODUCTION

Phosphate deposits of sedimentary origin are known to be associated with uranium and decay products of uranium series[1]. The world average uranium content in marine phosphorite deposits is estimated around 6-120 mg/kg. Mardin-Mazidag phosphate deposit is one of the most important phosphate deposits of sedimentary origin of Turkey[2]. The ore deposit lays around 200 km^2 areas at Mazi-mountain (Mazidag) of the southeast part of Anatolia. The wet chemical analysis[2] on 220 samples, obtained from Mazidag phosphate deposit, has indicated that the deposit contains 5-35 % P_2O_5, 1-4.1 % F and 15-137 mg/kg U. The mineralogical analysis of the samples indicated that the main phosphate mineral of the Mardin-Mazidag phosphate ores[2] are collophane (a massive colloidal variety of carbonate-flouroapatite) with a chemical composition of $[3Ca_3(PO_4)_2{\cdot}n(CaCO_3, F_2.O)X]$ and dahllite (carbonate-hydroxylapatite) which has the chemical formula $[3Ca_3(PO_4)_2{\cdot}CaCO_3]$. The aims of this study are to present IR

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vibrational and quantitative analyses results of the phosphate ore samples and to investigate the relations between P, U and F contents. In this study, quadratic regression model were applied on the uranium, phosphate and fluorine analyses results of 25 individual phosphate samples to show the interrelation between phosphate, uranium and fluorine concentrations.

EXPERIMENTAL

The composite sample (*ca.* 1 kg) representing the phosphate ores of Mardin-Mazidag phosphate deposit of Turkey was prepared as mixtures of the same proportions of 25 individual phosphate samples. The composite sample was dried (40 ºC) and ground to *ca.* 200 mesh size powder and homogenized, prior to analysis. The IR spectra (4000-400 cm^{-1}) of KBr disc of the composite sample was recorded on a Jasco 300E FT-IR spectrometer (2 cm^{-1} resolution) based on averaging 200 sample and 16 background scans. Spectroscopic manipulations such as baseline adjustment, smoothing and band component analysis were performed using spectracalc software package GRAMS/AI (Thermo Galactic, USA) In the case of band component analysis, band fitting was undertaken until reproducible results were obtained with squared correlations of r^2 greater than 0.999.

EDXRF analysis was performed by Spectro IQ EXRF spectrometer. About 4 g of dry sample powder and 0.9 g WAX, which were homogenized by grinding 5 min using a mixer mill, was pressed into 31 mm diameter pellets by using stainless steel Spex evacuable dies and 25 tons hydraulic press, for quantitative analysis. The samples were analyzed for 300 s using an air cooled low power Pd end window X-ray tube (25-50kV) combined with HOPG crystal for monochromatization and polarization of the primary tube spectrum. A silicon drift detector (SDD) was used to collect the fluorescence radiation from the sample. The resolution of the SDD was better than 175 eV (for Mn K_α at an input count rate of 10000 cps). During the measurement the excitation area was flushed with helium gas. The accuracy of the analytical procedures was checked against the standard reference materials.

In the case of regression analysis quadratic regression model[3] was applied and MATLAB 6.0 software was used.

RESULTS AND DISCUSSION

The analytical results of the composite sample and U, F and P analysis results of the individual phosphate samples from which composite sample has been prepared, are given in Tables 1 and 2, respectively. In order to investigate interrelations between P_2O_5 (%), U (mg/kg) and F (%) concentrations of the phosphate ore samples, the regression analysis based on the analysis were performed and the results are given in Table-2.

TABLE-1
CONCENTRATIONS OF THE COMPOSITE SAMPLE COMPOSED 25 INDIVIDUAL PHOSPHATE ORE SAMPLES FROM MAZIDAG*

P_2O_5 (%)	23.00	Cl (mg/kg)	250
CaO (%)	49.50	U (mg/kg)	60
Al_2O_3 (%)	1.50	SO_3 (%)	0.58
MgO (%)	1.70	Y (mg/kg)	200
K_2O (%)	0.13	V (mg/kg)	300
Na_2O (%)	0.05	Cr (mg/kg)	200
SiO_2 (%)	10.50	Mn (mg/kg)	350
Fe_2 O_3 (%)	0.05	Ni (mg/kg)	200
TiO_2 (%)	0.01	Mo (mg/kg)	30
MnO (%)	0.01	LOI[b] (%)	9.6
F[a] (%)	3.00	–	–

*EDXRF results except where indicated; [a]Measured by distillation-colorimetry; [b]Loss on ignition (LOI), obtained by analytical measurement.

TABLE-2
U, F AND P_2O_5 ANALYSIS RESULTS OF THE 25 INDIVIDUAL PHOSPHATE SAMPLES*

No.	P_2O_5 (%)	U (mg/kg)	F (%)
1	30.32	44	3.23
2	32.63	63	3.85
3	33.08	60	3.90
4	21.26	32	2.21
5	31.34	55	3.44
6	33.00	61	3.58
7	25.63	44	2.62
8	29.28	51	3.15
9	23.30	49	2.29
10	35.33	51	4.15
11	21.23	40	2.44
12	28.20	33	3.25
13	23.20	30	2.58
14	23.14	44	2.08
15	8.43	3	0.89
16	17.05	16	1.71
17	9.37	9	1.04
18	6.57	5	0.69
19	7.60	7	0.81
20	4.61	6	0.40
21	4.50	4	0.45
22	27.92	47	3.06
23	8.30	7	0.86
24	34.02	68	3.30
25	33.65	61	3.00

*U and P_2O_5 results were obtained by EDXRF analysis F^- measured by distillation-colorimetry.

Regression analysis: The quadratic regression models[3] are one of the most widely used in practice. They allow description of the object in a comparatively wide area of the input variable change. They are expressed as follows:

$$\hat{y} = b_0 + \sum_{i=1}^{m} b_i x_i + \sum_{i=1}^{m} b_i x_i^2$$

where $\hat{y}$ is the response variable, b the regression coefficients of the model and x the coded levels of the independent variables. MATLAB 6.0 software was used for regression and graphical analysis.

Consider the real data consisting of 25 observations on y, the U concentration in mg/kg and two predictor variables x_1, x_2 that represent P_2O_5 and F concentrations in %, respectively. After the regression analysis for present experiment, the following mathematical model is obtained:

$$\hat{y} = -8.9614 + 3.0972x_1 - 10.1493x_2 \quad (1)$$

The statistical significance of the model eqn. 1 was evaluated by the F-test analysis of variance (ANOVA), which showed that this regression is statistically significant at all confidence level (significance; $F = 2.86 \times 10^{-13}$) The coefficient of determination of the model ($R^2 = 0.93$) was calculated to be indicating that 93 % of the variability in the response could be explained by the model. As a result the interrelation between P_2O_5, U and F concentrations of the phosphate ore samples could be expressed as follows

$$C_{U(mg/kg)} = -8.9614 + 3.0972\ C_{P_2O_5(\%)} - 10.1493\ C_{F(\%)} \quad (2)$$

where $C_{U(mg/kg)}$, $C_{P_2O_5(\%)}$, $C_{F(\%)}$ are U, P_2O_5 and F concentrations, respectively. The response surface described by the model eqn. 2 is given in Fig. 1.

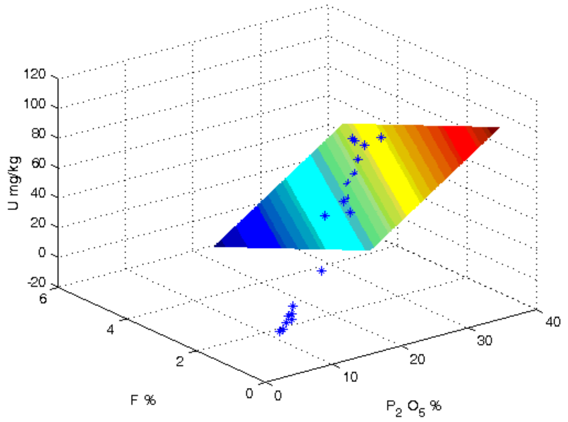

Fig. 1. Response surface described by the model eqn. 1 to estimate y (uranium in mg/kg) concentration over the independent variables x_1 (F %) and x_2 (P_2O_5)

The presence of uranium in phosphate deposits was explained by the replacement of some of the Ca^{2+} ions in the carbonate-florine-apatite structure by U^{4+} ions[2]. The present results are in accord with this proposal.

The IR spectrum of the composite phosphate ore sample was given in Fig. 2. The spectrum indicates presence of carbonate in addition of phosphate bands. Mineralogical analysis was indicated presence of calcite impurity in addition of main phosphate minerals, dahllite and collophane (carbonate-apatite structure). The band component analysis of the carbonate stretching region is given in Fig. 3. Seven bands are identified at 1536 vw, 1505 m, 1487 vw, 1471 m, 1456 ms, 1430 s, 1409 ms cm^{-1}. 1471, 1456 and 1409 cm^{-1} bands are in excellent agreement with published IR data for the carbonate stretching bands of collophane[4]. 1430, 1487 and 1505 cm^{-1} bands are assigned[4] to $CaCO_3$.

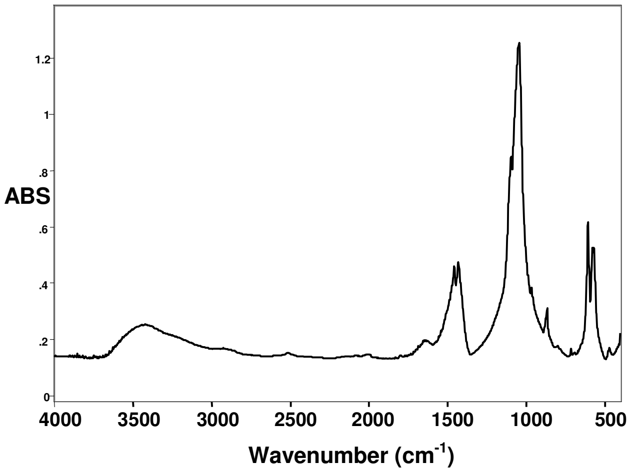

Fig. 2. FT-IR spectrum of the composite phosphate ore sample obtained from Mardin-Mazidag phosphate deposit

The band component analysis of the phosphate stretching region is given in Fig. 4. Seven bands have been observed, 1001 m, 964 w and 938 w, cm^{-1} bands are assigned to P-O symmetric stretching vibration (ν_1)[5,6] whereas, 1107 s, 1095 m, 1064 vs, 1040 vs cm^{-1} bands are assigned to antisymmetric stretching vibration (ν_3) of various phases of phosphate ion in phosphate ore deposit, that contain mainly collophane and dahllite mineral. These results are in agreement with previously published data on hydroxyl apatite and some basic phosphate minerals[5,6]. The IR spectrum of low wavenumber region of the composite sample is given in Fig. 5. The 692 vw, 604 vs, 576 s and 569 s cm^{-1} bands are assigned to out-of-plane bending vibration (ν_4) and 471 m and 422 w cm^{-1} bands to symmetric bending vibration (ν_2) of phosphates. 712 w cm^{-1} band is due to calcite impurity.

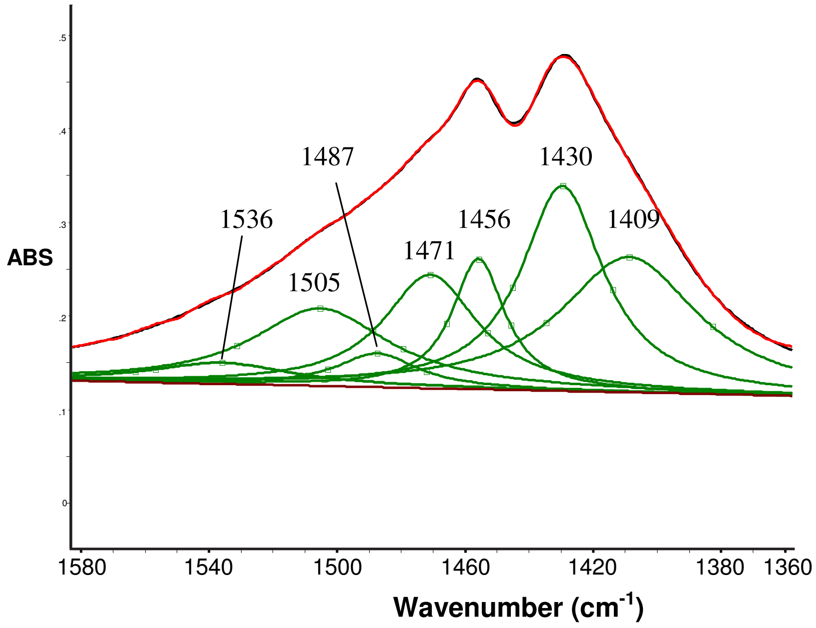

Fig. 3. Band component analysis of the 1560-1380 cm^{-1} region of the FT-IR spectrum of the composite phosphate ore sample

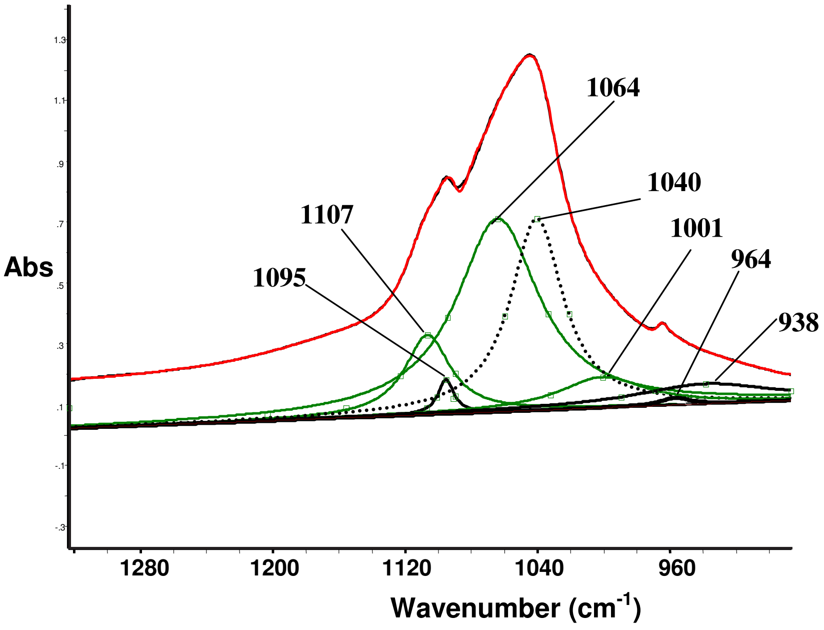

Fig. 4. Band component analysis of the 1320-900 cm^{-1} region of the FT-IR spectrum of the composite phosphate ore sample

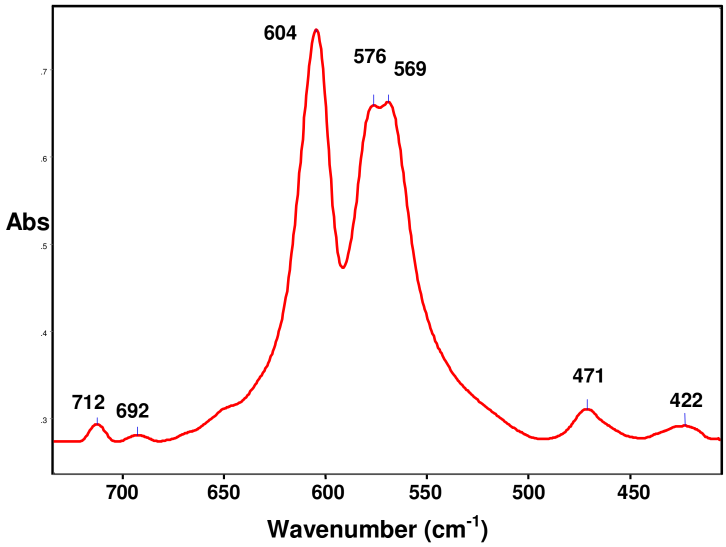

Fig. 5. FT-IR spectrum of the 725-400 cm^{-1} region of the composite phosphate ore sample

Conclusion

EDXRF and FT-IR spectral analyses of the composite sample of Mardin-Mazidag phosphate deposit, that compose of collophane and dahllite minerals were reported. IR spectral analysis enables us to characterize collophane and dahllite bands. The interrelation between the uranium, phosphate and fluorine contents of the ore samples were shown by quadratic regression analyses.

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