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Measurement of Trace Elements in KH_2PO_4 Crystals
by X-ray Fluorescence Spectrometry

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Measurement of Trace Elements in KH_2PO_4 Crystals by X-ray Fluorescence Spectrometry

Richard W. Ryon and Theresa I. Duewer

ABSTRACT

A non-destructive method is described for the quantitative measurement of impurities in KDP (KH_2PO_4) crystals. Part per million concentrations of impurities can be determined with good accuracy in about one hour of instrument time. An energy dispersive x-ray spectrometer is used. Both the crystals and the solutions from which they are grown may be analyzed.

INTRODUCTION

The laser fusion program is developing large KDP crystals for frequency doublers. It is imperative that impurity levels be kept very low for high efficiency functioning of the doublers. X-ray spectrometry and optical emission spectrometry are the two principal complimentary methods of analysis used to measure trace impurities in the crystals and raw materials. This report describes the x-ray fluorescence analysis.

We have presently chosen to use our energy dispersive spectrometer rather than our new wavelength dispersive spectrometer for most elements because:

1. The primary beam (excitation source) is easily filtered in the energy dispersive system. Filtering the X-ray tube spectrum with metal foils reduces the background under the peaks being measured, thereby giving better detection limits. Beam filtration is planned for the wavelength dispersive spectrometer, but the mechanism has not yet been installed.
2. The wavelength dispersive instrument requires specimen masks. High purity masks have not yet been obtained.

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3. The visual display of the x-ray spectrum with the energy dispersive system allows the analyst to "interact" with the data. The analyst can thus visually determine the presence or absence of impurity peaks and can best set positions for measuring the spectral background. Graphics have not yet been obtained for the wavelength dispersive instrument.

The operating characteristics of the energy dispersive spectrometer have previously been described.¹

EXPERIMENTAL CONDITIONS

Both liquid and solid samples are contained in "Spex" plastic cups, which are sealed with $\frac{1}{2}$ mil (6.4 μ M) Mylar film. The cups are inverted during analysis, with the measurements being made through the thin Mylar film; 4.0 ml of liquid is used.

Two excitation conditions are used for optimal sensitivity. In both cases, a standard side window, grounded anode tungsten x-ray tube is used.

1. For the elements Si-Fe, a .010" (.025 cm) copper filter is used. Tube conditions are 20 KV and 20 mA.
2. For the elements Fe-Mo, plus W, Ta, Pb, etc., a .020" (.051 cm) tin filter is used. Tube conditions are 35 KV and 35 Ma.

MEASUREMENTS AND CALCULATION OF CONCENTRATIONS

Analysis time is generally 2000 seconds (live time). The pulse height analyzer is set to .02 KeV/channel. Intensities are measured by integrating over 0.20 KeV (11 channels) centered on the $K\alpha$ or $L\alpha$ peak maxima. Background values are obtained at each peak by linear interpolation.

Irregular and non-standard crystal surface areas are compensated for by normalizing the net peak intensities using the $K K\alpha$ line. The corrected (normalized) intensities are calculated by

$$I_{\text{corr}} = I_{\text{meas}} \times \frac{I(K K\alpha \text{ standard})}{I(K K\alpha \text{ unknown})}$$

No such correction is necessary for liquids.

The concentrations of impurities are obtained by comparison to prepared standards. At trace levels, intensities are linear functions of concentrations:

$$C_i = K_i I_i.$$

Calibration constants are given in Table 1 for KDP crystals, and in Table 2 for saturated KDP solutions.

STANDARDIZATION

1. KH_2PO_4 solids (crystals).

Weighed amounts of pure element oxides or carbonates were added to KH_2PO_4 , thoroughly mixed and pelletized.

2. KH_2PO_4 saturated solutions.

Different volumes of atomic absorption standards were added to 4 ml of sat. KH_2PO_4 solution. (The atomic absorption standards were purchased from Alpha Analytical Laboratories, Jersey City, N.J.)

Individual values of the calibration constants are obtained from least squares quadratic fits to the data (log (ppm/cps) vs. atomic number). The data and the fitted curves for KDP crystals are shown in Figures 1 and 2, and for solutions in Figure 3.

COMPARISON TO EMISSION SPECTROSCOPY RESULTS

The concentrations obtained by x-ray fluorescence are in close agreement with those obtained by optical emission spectroscopy where there are overlapping measurements. The two methods compliment each other, as each has its strong and weak points in the periodic table of elements. A typical analysis is given in Table 3.

TABLE I
KH₂PO₄ Crystal Sensitivity Factors

<u>Element</u>	<u>Filter</u>	<u>ppm/cps</u>
Al	Copper	
Se	"	
P	"	
S	"	
Cl	"	
K	"	179
Ca	"	118
Ti	"	53
Cr	"	25
Mn	"	17.2
Fe	"	12.1
K	Tin	3061
Fe	"	171
Ni	"	86
Cu	"	62
Zn	"	46
As	"	20
Rb	"	8.3
Sr	"	6.9
Pb	"	28.8

TABLE 2
KH₂PO₄ Sat. Solution Sensitivity Factors

<u>Element</u>	<u>Filter</u>	<u>ppm/cps</u>
K	Cu	3510
Ca	"	1230*
Ti	"	308*
Cr	"	54.5
Mn	"	14.2
Fe	"	7.88

*extrapolated from fitted data.

TABLE 3
Typical KH_2PO_4 Analysis*

Element	#130		#131	
	<u>X-ray</u>	<u>E. S.</u>	<u>X-ray</u>	<u>E. S.</u>
Ti	15	<3	10	4
Cr	2		<1	
Fe	10	7	<4	4
Zn	10		<2	
Rb	<0.5	1	<0.5	1
Mo	<1	<3	<1	<3
Na		3		3
Mg		2		1
Al		10		30
Si		15		10
Ca		5		<4
Cs		10		10
Cd, Sb, Sn		<30		<30
Nb	<1	40	<1	<10
B, Ba, Bi	}	<3		<3
Ni, Pb, Sn				
Ti				

* Units = $\mu\text{g/g}$

Figure 1

Figure 2

Figure 3

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