

An X-ray diffraction method for semiquantitative mineralogical analysis of Chilean nitrate ore

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ABSTRACT

Computer analysis of X-ray diffraction (XRD) data provides a simple method for determining the semiquantitative mineralogical composition of naturally occurring mixtures of saline minerals. The method herein described was adapted from a computer program for the study of mixtures of naturally occurring clay minerals. The program evaluates the relative intensities of selected diagnostic peaks for the minerals in a given mixture, and then calculates the relative concentrations of these minerals. The method requires precise calibration of XRD data for the minerals to be studied and selection of diffraction peaks that minimize inter-compound interferences. The calculated relative abundances are sufficiently accurate for direct comparison with bulk chemical analyses of naturally occurring saline mineral assemblages.

Key words: X-ray diffraction, Semiquantitative, Nitrate ore, Chile.

RESUMEN

Método para el análisis mineralógico semicuantitativo de nitratos chilenos por difracción de rayos X. El análisis por difracción de rayos X (XRD) es un método simple que se puede utilizar para determinar la composición mineralógica semicuantitativa de mezclas de minerales salinos que ocurren en forma natural. El método descrito en el presente estudio fue adaptado de un programa computacional para el estudio de mezclas de minerales de arcilla. El programa evalúa las intensidades relativas de picos de diagnóstico seleccionados para minerales de una mezcla determinada y, enseguida, calcula las concentraciones relativas de estos minerales. El método requiere una calibración precisa de los datos XRD para los minerales que serán estudiados, seleccionándose los picos de difracción que minimizan las interferencias interminerales. Las abundancias relativas calculadas son suficientemente precisas para la comparación directa con análisis químicos de diversas asociaciones de minerales salinos.

Palabras claves: Difracción de rayos X, Semicuantitativo, Nitratos, Chile.

INTRODUCTION

A computerized X-ray diffraction (XRD) method for semiquantitative mineralogical analysis was developed to provide reliable and rapid mineralogical

compositions for Chilean nitrate ore samples. The computer program used is adapted from the program of Hosterman and Dulong (1989), and is available

on an anonymous FTP server¹. The method is based on laboratory study of mixtures of a selected group of synthetic and natural saline minerals that are amongst the most common constituents of the Chilean nitrate ores, to determine the percentages of each mineral in such deposits. These ores are complex both mineralogically (Table 1) and chemically (Table 2). The minerals studied were synthetic, reagent-grade nitratine [NaNO_3], halite [NaCl], and niter [KNO_3] and high-purity, natural darapskite

[$\text{Na}_3(\text{NO}_3)(\text{SO}_4)\cdot\text{H}_2\text{O}$], blodite [$\text{Na}_2\text{Mg}(\text{SO}_4)_2\cdot 4\text{H}_2\text{O}$], and gypsum [$\text{CaSO}_4\cdot 2\text{H}_2\text{O}$], which represent the three major anions, NO_3^- , Cl^- , and SO_4^{2-} , in the saline minerals of the Chilean nitrate deposits (Tables 1 and 2). Major concerns of the study were the identification and quantification of the minerals present in the mixtures, determination of the extent of interference among the diffraction peaks of the various saline minerals, and the effect of such interferences on the reliability of the method.

TABLE 1. CHEMICAL COMPOSITION OF SALINE MINERALS IN THE CHILEAN NITRATE DEPOSITS, AND CORRESPONDING JOINT COMMITTEE ON POWDER DIFFRACTION STANDARDS (JCPDS) FILE NUMBERS.

JCPDS No. (1996)	MINERAL
HALIDES	
5-0628	Halite, NaCl
NITRATES	
36-1474	Nitratine, NaNO_3
5-0377	Niter, KNO_3
23-1408	Darapskite, $\text{Na}_3(\text{NO}_3)(\text{SO}_4)\cdot\text{H}_2\text{O}$
21-0682	Humberstonite, $\text{K}_3\text{Na}_7\text{Mg}_2(\text{SO}_4)_6(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$
SULFATES	
37-1465	Thenardite, Na_2SO_4
11-0647	Mirabilite, $\text{Na}_2\text{SO}_4\cdot 10\text{H}_2\text{O}$
19-1187	Glauberite, $\text{Na}_2\text{Ca}(\text{SO}_4)_2$
19-1215	Blodite, $\text{Na}_2\text{Mg}(\text{SO}_4)_2\cdot 4\text{H}_2\text{O}$
33-0882	Kieserite, $\text{MgSO}_4\cdot\text{H}_2\text{O}$
36-0419	Epsomite, $\text{MgSO}_4\cdot 7\text{H}_2\text{O}$
33-0311	Gypsum, $\text{CaSO}_4\cdot 2\text{H}_2\text{O}$
37-1496	Anhydrite, CaSO_2
IODATES AND CHROMATES	
28-0221	Lautarite, $\text{Ca}(\text{IO}_3)_2$
26-1405	Brüggenite, $\text{Ca}(\text{IO}_3)_2\cdot\text{H}_2\text{O}$
46-1278	Hectorfloresite, $\text{Na}_9(\text{IO}_3)(\text{SO}_4)_4$
25-0132	Dietzeite, $\text{Ca}_2(\text{CrO}_4)(\text{IO}_3)_2$
5-0365	Tarapacaite, K_2CrO_4
27-0380	Lopezite, $\text{K}_2\text{Cr}_2\text{O}_7$
.	Fuenzalidaite $\text{K}_6(\text{Na},\text{K})_4\text{Na}_6\text{Mg}_{10}(\text{SO}_4)_{12}(\text{IO}_3)_{12}\cdot 12\text{H}_2\text{O}$
.	Carlosruizite $\text{K}_6(\text{Na},\text{K})_4\text{Na}_6\text{Mg}_{10}(\text{SeO}_4)_{12}(\text{IO}_3)_{12}\cdot 12\text{H}_2\text{O}$
BORATES	
2-0419	Ulexite, $\text{NaCaB}_5\text{O}_9\cdot 8\text{H}_2\text{O}$
2-0420	Probertite, $\text{NaCaB}_5\text{O}_7(\text{OH})_4\cdot 3\text{H}_2\text{O}$
8-0116	Ginorite, $\text{Ca}_2\text{B}_{14}\text{O}_{23}\cdot 8\text{H}_2\text{O}$
35-0646	Hydroboracite, $\text{CaMg}(\text{B}_3\text{O}_4(\text{OH})_3)_2\cdot 3\text{H}_2\text{O}$
18-669	Kaliborite, $\text{KHMg}_2\text{B}_{12}\text{O}_{16}(\text{OH})_{10}\cdot 4\text{H}_2\text{O}$
39-0358	Iquiqueite, $\text{K}_3\text{Na}_4\text{Mg}(\text{CrO}_4)\text{B}_{24}\text{O}_{39}(\text{OH})\cdot 12\text{H}_2\text{O}$

* Ericksen *et al.* (1994).

¹ Available on National Coal Resources Data Systems (NCRDS) anonymous server IP: 192.58.223.1, directory:/pub/xrd. Files: executable (.exe), mineral library (.lib), sample data file (SAMPLE), and seven Fortran 77 source files (.for).

TABLE 2. BULK CHEMICAL COMPOSITION (WT.%) OF WATER-SOLUBLE SALINE CONSTITUENTS IN TYPICAL NITRATE ORES AND HIGH-PURITY VEINS OF CHILEAN NITRATE DEPOSITS, FROM ERICKSEN (1981).

	1	2	3	4	5	6
NO ₃	6.35	6.66	12.11	17.67	72.15	32.63
Cl	3.87	7.07	7.15	11.11	.07	21.84
SO ₄	8.6	12.43	14.23	3.47	.1	8.3
IO ₃	.061	.068	.05	.004	-	.04
CrO ₄	.035	.027	.02	-	.04	.25
BO ₃	.54	.92	.13	.11	-	.27
Na	6.2	8.9	9.2	13.8	26.7	26
K	.56	.61	.46	.95	-	.32
Mg	.15	.73	1.06	-	.01	.93
Ca	1.15	2.27	1.61	1.06	.05	.32
H ₂ O	1.74	1.08	1.03	1.87	1.52	3.4
Insoluble	72	59	47	50	0	4

¹ Average grade of 5.97 million metric tons of ore treated at Oficina Pedro de Valdivia, July 1, 1935-June 30, 1936; ² Average grade of 6.27 million metric tons of ore treated at Oficina Maria Elena, July 1, 1951-June 30, 1952; ³ Average grade of hand-selected nitrate ore treated by Oficina Alemania during the month of February, 1951; ⁴ Sample of high-grade nitrate ore from Oficina Humberstone; ⁵ High-purity NaNO₃ ('caliche blanco') vein at Oficina Lautaro.

⁶ High-purity 'caliche blanco' vein at Oficina Santa Fe; - not detected

By far, the most abundant minerals in typical nitrate ore are nitratine and halite; each of the sulfate minerals listed in table 1 may be dominant locally, but typical ore generally contains two or more sulfate minerals, neither of which is as abundant as either nitratine or halite even though the total SO₄ might be greater than either NO₃ or Cl (Table 2). In addition, typical nitrate deposits contain trace amounts, generally less than 0.1%, of the anions IO₃⁻, CrO₄²⁻, and several borate minerals (Tables 1 and 2).

The relationship between mineralogical and chemical composition is essential to understanding

the solution chemistry of the complex saline deposits and the development of models for the phase systems in which the nitrate ores formed. Although several partial phase systems involving the major anions of the ores have been studied, no effort has been made to develop an overall model for the deposits such as that for oceanic saline deposits that was first defined on the basis of experimental data by Van't Hoff (Braitsch, 1971). Such a model is not only important to a better understanding of the nitrate deposits but also would have direct application to the beneficiation of nitrate ores.

SAMPLE PREPARATION AND INSTRUMENTAL

Three groups of samples were prepared for XRD analysis: 1- pure minerals to calibrate for mineral identification; 2- mixtures of known, predetermined composition analyzed for semiquantitative calibration; 3- mixtures of known, predetermined composition analyzed as unknown. For descriptions of these mixture compositions, refer to Jackson and Erickson (1994), tables 3 and 4. Samples were prepared from pure mineral compounds which were dried in an oven at 50°C for 4 hours to remove excess moisture, and then pulverized in an agate mortar and sieved to <200 mesh. All mixtures were prepared by weighing predetermined amounts of

the pure mineral compounds to an accuracy of ±0.0005 g, and then mixing these components first in an agate mortar and then in a shaker mill. Two pressed pellets for XRD analysis were made for each sample on a backing of 50% each of boric acid and methyl cellulose using a hydraulic press. Each pellet was analyzed at least once, accounting for at least two analyses for each sample. To test more accurately for precision, two additional pellets were analyzed 5 times, for a total of 10 analyses each. A summary of the resulting accuracy and precision analyses are shown in table 3. The complete precision and accuracy data, as well as report sheets showing

XRD results in detail for calibration mixture analyses and pure mineral standard analyses, are shown in Jackson and Ericksen (1994), tables 5-7, and 9, respectively.

The XRD analyses were made with a Diano² computer-automated X-ray diffraction unit, with a spinning sample holder. The digitized X-ray data

were collected on an IBM² PC every 0.02° 2 θ , for 0.95 seconds per step, starting at 3.00° and ending at 60.00°. Copper K-alpha radiation was used with the following optical settings: a 1° soller slit, a 0.1° detector slit, a graphite monochromator, and a 2° take-off angle.

TABLE 3. SUMMARY OF TESTS FOR RELIABILITY OF COMPUTER CALCULATED MINERAL COMPOSITIONS BASED ON X-RAY DIFFRACTION DATA FOR MIXTURES OF SALINE MINERALS.

Mineral	Average absolute difference	Average standard deviation (1 σ)	Number of sample aliquots	Number of analytical determinations
Nitratine	1.3%	1.1	34	50
Halite	1.3%	1	26	42
Niter	2.3%	1.6	8	16
Darapskite	1.0%	0	6	14
Gypsum	1.3%	0.9	8	16
Blodite	1.8%	0.5	8	16

THE COMPUTER PROGRAM

The computer processing of the X-ray data, which is described in detail by Hosterman and Dulong (1989), is based on algorithmic calculation of the digitized X-ray data representing the diffraction pattern. Briefly, the program smoothes the digitized data, determines and subtracts background, identifies and locates peak positions and integrates peak (area) intensities, qualitatively identifies the mineral associated with the peaks, and estimates weight percentages of each mineral present.

The user must supply both a sample file containing a digitized XRD pattern of an unknown mineral mixture, and a library file consisting of XRD data for the minerals likely to be encountered in the sample (Table 4). The authors have used only six of the major minerals present in nitrate ore in developing the method. A more comprehensive study of complex saline ores, such as the Chilean nitrate ores, will require a library file containing all the minerals likely to occur in amounts detectable by X-ray diffraction. The output of the program consists of 2 θ and d-spacing values, relative intensities for each peak, the minerals determined to be present, and estimates of the relative weight percentages of each mineral.

The library file used in this study (Table 4) contains selected XRD data for the six minerals used to develop and test the method and instrument settings as defined by Hosterman and Dulong (1989). All variables shown in this library file were used for this study and are in the precise format as required by the program to function, any deviation from this format may incur error. Important variables include the window of acceptability, the multiplication factor (also called reference intensity ratios), and the number of major peaks to be used for mineral identification. The window of acceptability is adjusted to compensate for errors in instrumental precision by defining the number of degrees 2 θ from the published peak position (Joint Committee on Powder Diffraction Standard, 1996) that the program will search for a positive match for that peak. This is essential for defining major peaks that are in close proximity to each other. The multiplication factor or strength factor is used to calculate mineral concentrations; it is adjusted so that the mineral concentrations calculated reflect the known values of the calibration standard for that mineral.

² Any use of trade names in this paper is for descriptive purposes only, and does not imply endorsement by the U.S. Geological Survey.

TABLE 4. COMPUTER PRINTOUT OF THE LIBRARY FILE OF X-RAY DIFFRACTION DATA REQUIRED FOR MINERAL IDENTIFICATION AND CALCULATION OF COMPOSITION OF MINERAL MIXTURES. THE FILE IS IN THE FORMAT AS REQUIRED BY THE PROGRAM OF HOSTERMAN AND DULONG (1989).

Darapskite¹		29.0²	.700³	33⁴	500⁵	1⁶	10,000⁷						
10.3 ⁸	100 ⁹	TT ¹⁰	4.13		7	FF	3.59	2	FF	3.53	4	FF	
3.46	9	FF	3.27		3	FF	3.19	2	FF	3.08	1	FF	
2.955	1	FF	2.856		8	FF	2.667	1	FF	2.594	8	FF	
2.534	1	FF	2.438		2	FF	2.421	1	FF	2.378	1	FF	
2.341	1	FF	2.251		1	FF	2.177	1	FF	2.100	1	FF	
2.072	5	FF	2.013		1	FF	1.938	1	FF	1.912	1	FF	
1.773	4	FF	1.748		1	FF	1.728	2	FF	1.705	1	FF	
1.673	1	FF	1.629		1	FF	1.595	1	FF	1.580	1	FF	
1.540	1	FF											
Halite		74.6	.500	5	200	1	5,000						
3.26	3	FF	2.821		100	FF	1.994	20	TT	1.701	1	FF	
1.628	5	FF											
Nitratine		16.9	.700	10	200	1	10,000						
3.894	2	FF	3.038		100	TT	2.806	20	FF	2.537	3	FF	
2.312	9	FF	2.125		4	FF	1.897	21	FF	1.880	4	FF	
1.652	2	FF	1.628		2	FF							
Niter		62.5	.300	23	500	1	840						
4.66	14	FF	4.58		4	FF	3.78	100	FF	3.73	17	TT	
3.033	70	FF	2.763		34	FF	2.707	11	FF	2.647	87	FF	
2.409	4	FF	2.367		3	FF	2.332	5	FF	2.292	1	FF	
2.192	27	FF	2.159		17	FF	2.071	9	FF	2.050	16	FF	
1.947	34	FF	1.888		2	FF	1.750	4	FF	1.733	1	FF	
1.707	3	FF	1.688		4	FF	1.585	5	FF				
Gypsum		69.5	.500	25	200	1	3,300						
7.63	100	TT	4.283		12	FF	3.799	15	FF	3.065	18	FF	
2.873	4	FF	2.789		1	FF	2.685	4	FF	2.597	1	FF	
2.534	1	FF	2.495		1	FF	2.452	1	FF	2.406	1	FF	
2.219	3	FF	2.074		3	FF	2.048	1	FF	1.992	1	FF	
1.899	6	FF	1.879		1	FF	1.811	3	FF	1.778	3	FF	
1.684	1	FF	1.645		1	FF	1.620	3	FF	1.600	1	FF	
1.584	1	FF											
Blodite		50.1	.200	41	500	1	1,300						
4.555	100	TT	4.442		1	FF	4.281	20	FF	4.126	6	FF	
3.981	4	FF	3.860		4	FF	3.800	13	FF	3.333	17	FF	
3.289	89	FF	3.252		30	FF	3.091	1	FF	3.055	1	FF	
2.971	25	FF	2.724		36	FF	2.687	8	FF	2.644	26	FF	
2.586	12	FF	2.518		1	FF	2.454	2	FF	2.420	1	FF	
2.314	7	FF	2.297		6	FF	2.271	9	FF	2.194	4	FF	
2.170	10	FF	2.141		3	FF	2.113	7	FF	2.062	1	FF	
2.025	11	FF	1.933		13	FF	1.921	6	FF	1.901	2	FF	
1.858	7	FF	1.779		15	FF	1.753	2	FF	1.723	2	FF	
1.711	1	FF	1.665		8	FF	1.661	9	FF	1.601	4	FF	
1.567	6	FF											
End of Library										99999			
.5 ¹¹	1.0 ¹²	.02 ¹³	3.00 ¹⁴	60.00 ¹⁵	0 ¹⁶								
	0263 ¹⁷	0656	0694	1200	1275			4000					
1.5, 3.5, 4.0 ¹⁸													

¹ Mineral name; ² Mass absorption coefficient; ³ Window of acceptability; ⁴ Number of peaks; ⁵ Minimum intensity; ⁶ Number of important peaks; ⁷ Multiplication factor; ⁸ d-spacing; ⁹ Relative intensity; ¹⁰ Code describing peak importance: TT= most important; FF= less important; ¹¹ Instrument factor; ¹² Goniometer speed in degrees 2 θ /min (1.0); ¹³ 2 θ counting interval (0.02); ¹⁴ Lowest 2 θ angle (3.00); ¹⁵ Highest 2 θ angle (60.00); ¹⁶ Code for chemistry calculation (0=no); ¹⁷ Digital count numbers where doublets are expected (0263, 0656, 0694, 1200, 1275, 4000); ¹⁸ T1, T2, T3 peak tests (T1= 1.5, T2 = 3.5, T3 = 4.0). Test factors T1 and T2 test the validity of a valley between two peaks, and T3 is used to reject broad, weak, high angle peaks.

For this study, six calibration standards were prepared to calibrate the strength factors used in the library file. One calibration sample was prepared as a mixture of 50% each of NaNO_3 and NaCl ; the other 5 calibration samples were prepared as mixtures of 95% NaNO_3 and 5% of the mineral being standardized. In this way, the calibration assured the greatest accuracy at the 5% level, relative to nitratine, for niter, darapskite, gypsum, and blodite, which commonly are present in low concentrations in the Chilean nitrate ores, and at the 50% level for halite that which, together with nitratine, is generally one of the most abundant constituents of the nitrate ores.

Pure mineral standards for the six minerals used in this study were analyzed twice each (Jackson and Ericksen, 1994, Table 9) to determine 2θ and peak intensities used in the library file. The XRD data were, then, computer adjusted to the position of a known peak selected from published X-ray data for the given mineral (JCPDS, 1996) to compensate for instrumental error. It is important that this adjustment be made only after the identities of the minerals to be

quantified are verified. Intermediate compositions of a solid solution series may yield XRD results that are shifted with respect to peak positions of end member compositions. It is important that only instrument error be compensated for by this adjustment. The 2θ values for the specific peaks used for this adjustment are shown in Jackson and Ericksen (1994), tables 8 and 9. The computer generated d-spacing and intensity data of the pure mineral standards were then compared with published values (Joint Committee on Powder Diffraction Standard, 1996), and those peaks that were consistently resolved and identified by the computer program were matched with published d-spacings, and these published values were entered into the computer library file. The averages of the measured intensity ratios for the two analyses of each mineral were also entered into the library file. The measured intensities were used, rather than published intensities, to compensate for possible effects of sample orientation in the pressed powder mounts that could have the effects of enhancing or diminishing peak intensities.

DISCUSSION OF RESULTS

Nitratine. Because nitratine is the most abundant and economically important nitrate mineral in the Chilean nitrate deposits, reagent-grade NaNO_3 was used as the primary component of the mixtures used in this study. The analyses of all samples containing nitratine were computer adjusted to the strongest peak at $2\theta = 29.45^\circ$ ($d = 3.038\text{\AA}$). This peak was also used as the primary identification peak for nitratine. Analyses of 34 samples containing nitratine as a major component showed an average absolute difference of $\pm 1.3\%$ between weighed and calculated concentrations of nitratine (Table 3).

Halite. Along with nitratine, halite is generally the most abundant saline mineral in the typically Chilean nitrate ores. To reflect this abundance, reagent-grade NaCl was mixed in equal proportions with NaNO_3 for all mixtures containing 3 or more minerals. The XRD analysis of pure NaCl was computer adjusted to the strongest peak at $2\theta = 31.70^\circ$ ($d = 2.821\text{\AA}$). However, because the computer program could not distinguish between this peak and an overlapping strong peak for nitratine, in mixtures of halite and nitratine, the next strongest peak for halite at $2\theta = 45.45^\circ$ ($d = 1.994\text{\AA}$) was used

as the primary identification peak for halite. This peak does not interfere significantly with any of the strong peaks of the other minerals studied. Semi-quantitative XRD analyses of halite in 26 samples showed an average absolute difference of $\pm 1.3\%$ between weighed and calculated concentrations of halite (Table 3).

Niter. Among the saline minerals occurring in minor amounts in Chilean nitrate ores, niter is important economically, because it is a source of both nitrate and potassium, the latter being utilized in the preparation of a potassium-rich nitrate product that commands a premium price as a fertilizer. However, although niter is widespread in Chilean nitrate ores, it does not occur in all ores and, where it does occur, it rarely exceeds 5% of the total saline material present.

Reagent-grade KNO_3 was used for this study, and the XRD analyses of the pure material were computer adjusted to the strong peak at $2\theta = 29.45^\circ$ ($d = 3.033\text{\AA}$). However, this is the same peak position as the strongest peak for nitratine, and the strongest peak for niter at $2\theta = 23.52^\circ$ ($d = 3.78\text{\AA}$) is interfered with by nearby peaks of moderate intensity for

blodite and gypsum, and was not resolved by the program if either of these minerals were present in mixtures containing at least 5% niter. Consequently, the nearby peak at $2\theta = 23.84^\circ$ ($d = 3.73\text{\AA}$), having an $I/I^\circ = 17$ in this study, was used as the primary identification peak for niter.

A concern with the identification of niter was whether the computer program would accurately and precisely resolve the peaks at $d = 3.73\text{\AA}$ and $d = 3.78\text{\AA}$. It was found that the two peaks were resolved down to the 5% level of niter in mixtures, but were not resolved in a mixture containing 1% niter and 99% nitratine (these results not shown). However, it was found that by decreasing the sampling interval from 0.02° to 0.01° 2θ , and thus effectively enhancing sensitivity to the detection of proximate peaks, the computer program did resolve them. Obviously, a slower goniometer speed would be desirable for XRD analyses of minor minerals in mixtures, but such a slower speed would double the time required for an analysis and it was not deemed necessary in this preliminary study. Semiquantitative XRD analyses for niter in eight samples showed an average absolute difference of $\pm 2.3\%$ between weighed and calculated concentrations of niter (Table 3).

Darapskite. The nitrate-sulfate mineral darapskite is a widespread, relatively minor but locally abundant constituent of the Chilean nitrate ores. It is one of the most abundant sulfate-bearing minerals in the Chilean ores because thenardite [Na_2SO_4], which is abundant in nearly all other continental saline deposits, is not stable in solutions from which NaNO_3 precipitates (Ericksen and Mrose, 1970) whereas darapskite is stable. Darapskite also presents a problem in beneficiation of nitrate ore because separation of pure NaNO_3 requires close control of solution chemistry to inhibit precipitation of darapskite, which is an undesirable contaminant.

The darapskite used in this study is natural crystalline material from the Chilean nitrate deposits. The XRD analyses of pure darapskite were computer adjusted to the relatively minor peak at $2\theta = 28.96^\circ$ ($d = 3.08\text{\AA}$), which was chosen because of several peaks tested, this peak gave the most consistent results. Nevertheless, the primary identification peak selected for darapskite was the strongest peak at $2\theta = 8.58^\circ$ ($d = 10.3\text{\AA}$). This peak does not interfere with any of the other peaks of the minerals studied. In an earlier study, it was shown that in mixtures of halite and darapskite, darapskite in amounts of as

little as 0.25% could be identified in XRD patterns (Ericksen and Mrose, 1970). Semiquantitative XRD analyses of six darapskite-bearing samples showed an average absolute difference of $\pm 1\%$ between weighed and calculated concentrations of darapskite (Table 3).

Blodite. Blodite is a widespread minor, but locally abundant sulfate mineral in the Chilean nitrate deposits. It is one of the principal sources of sulfate and magnesium in nitrate ore (Table 2). The blodite used in this study consists of pure crystalline material from a 10-15 cm wide vein in the oxide zone of a small silver and base-metal deposit near the town of Sierra Gorda, northern Chile. The XRD analyses of pure blodite were computer adjusted to the peak at $2\theta = 20.71^\circ$ ($d = 4.281\text{\AA}$), whereas the peak at $2\theta = 19.47^\circ$ ($d = 4.555\text{\AA}$) was selected as the primary identification peak. A relatively narrow window of acceptability was entered in the library file (Table 4) because of the close proximity of a niter peak at $d = 4.58\text{\AA}$. However, because of this narrow window of acceptability, only about 83% of the peaks in pure blodite was identified by the computer program. Semiquantitative XRD analyses of eight samples containing blodite showed an average absolute difference of $\pm 1.8\%$ between weighed and calculated concentrations of blodite (Table 3).

Gypsum. The chemical analyses of Chilean nitrate ores generally report only the saline constituents that are dissolved by hot water. As a consequence, relatively insoluble minerals in nitrate ore such as gypsum and anhydrite are reported incompletely by these chemical analyses. Inasmuch as these minerals are among the most abundant saline minerals in the nitrate deposits, chemical analyses requiring dissolution by hot water are misleading in terms of both chemical and mineralogical composition of these deposits. Obviously, XRD analyses offer a relatively simple method for determining the concentrations of such minerals.

The gypsum used in this study is from naturally occurring large crystals of selenite from Minas Gerais, Brazil. The XRD analyses of this pure gypsum were computer adjusted to the peak at $2\theta = 11.58^\circ$ ($d = 7.63\text{\AA}$). This peak was also used as the primary identification peak for gypsum, because it did not interfere with peaks of any other minerals studied. The average absolute difference between weighed and calculated concentrations of gypsum in eight samples analyzed semiquantitatively by XRD was $\pm 1.3\%$ (Table 3).

CONCLUSIONS

Semiquantitative mineralogy by computer analysis of X-ray diffraction data is a relatively rapid and reliable method for determining the concentration of saline minerals in mixtures. The overall accuracy of the method, determined by comparing the absolute differences between weighed and calculated values, showed an average absolute difference of $\pm 1.5\%$ relative to the weighed values. The overall precision of the method, described in terms of one standard deviation as a percentage of the mean, was $\pm 1\%$ absolute. The lower limit of concentrations studied was 5%, but this can be effectively reduced by decreasing the sampling interval.

A primary limiting factor for this semiquantitative method of mineral analysis is peak overlap, which can be minimized in several ways. First, the window of acceptability in the computer library file may be adjusted to better resolve peaks in close proximity. Furthermore, integration of as many peaks as possible minimizes the net effect that two particular overlapping peaks will have on the semiquantitative determinations. For mineral identification, however, it is recommended that a single peak be used if possible. This peak does not necessarily have to be the strongest peak for a given mineral, but it must be

free of interfering peaks of other minerals, and must have sufficient intensity to be resolved at the lower limit of detectability for the specific mineral.

For samples of a more complex matrix, particularly where single peaks for mineral identification cannot be clearly identified due to peak overlap, more complex approaches such as full-pattern profile fitting or Rietveld methods, may offer higher precision (Snyder and Bish, 1989).

The relationship between relative intensity (I/I^0) of a given peak for a mineral in a series of mixtures and its actual concentration in those mixtures is not necessarily linear, particularly in complex mineral mixtures where absorption effects are enhanced. Therefore, it is not practical to construct a simple linear regression to predict actual concentrations for a mineral based on relative intensity for a single peak. Calibrating for many peaks from the measurements of prepared mixtures compensates for these effects.

Inasmuch as the relative accuracy of the analyses decreases with the amount of mineral present in the sample, it is necessary that the method be calibrated for still lower concentrations, and a detection limit be determined for each of the minerals studied.

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