PITFALLS IN X-RAY DIFFRACTION METHODS OF ANALYSIS FOR IMPURITIES IN TALC POWDERS

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As we are all aware, the current high interest in potential and real health hazards of asbestos has resulted in a great number of investigations dealing with the isolation and identification of asbestos from a tremendous variety of manufactured, natural, and by-product materials. One effect of the great attention being given to asbestos minerals is to convey the erroneous impression that the predominant occurrence of serpentines and amphiboles are as the asbestos varieties. Rather special geological conditions seem to be required to produce asbestos (Vermaas, 1952), and it is fact that less than 1% of the world occurrences of serpentines and amphiboles are as the asbestos varieties (Thompson, 1973; Ampian, 1976).

INTERPRETATION ERRORS

Since asbestos is in fact somewhat rare, it is important to be certain that the identification of asbestos in a sample is correct. Certain pitfalls in the identification of asbestos and other minerals have become apparent, as follows:

Powder x-ray diffractometry is incapable of determining the morphological variety of a mineral. For example, examination of a powder x-ray diffractogram of essentially pure serpentine cannot unequivocally identify the sample to be a particular morphological variety. Preparation

of synthetic calibration standards using asbestos and talc, for example, has the tendency to bias the interpretation when analyzing real samples.

Examination of x-ray diffraction photographs of the tiniest asbestos fiber that can be handled shows that the pattern is streaked, indicating that the smallest fiber is still composed of multiple crystals oriented with slight displacements around the fiber axis (Hutchinson, et. al., 1975; Chisholm, 1973). Thus, single crystal x-ray diffraction does give some information as to whether or not the specimen could be asbestos.

Amphiboles

The amphibole family of minerals is characterized by similar crystal structure and wide variation in chemical composition and appearance. The name is derived from the Greek "amphibolos", meaning ambiguous, a most appropriate name since reliable identification of members of the group is indeed difficult. All amphiboles have x-ray diffraction patterns which are similar and are characterized by having their (110) or (210) diffraction peaks within ±0.2Å of each other (Table 1).

Selection of JCPDS Card No. 13-437 for tremolite ($d_{(110)}$ = 8.38Å = 10.56° 2θ for CuKα) as being representative and definitive for identification and quantification of that mineral presents problems which become apparent with examination of Table 1. Twenty-nine different JCPDS amphiboles have their (110) or (210) peaks within ±0.1° 2θ of this tremolite $d_{(110)}$ peak. Identification of an amphibole as being tremolite on the basis of a peak at 10.56° 2θ obviously is an identification with very low reliability. With further examination of Table 1, it becomes apparent that attempted

identification of any amphibole on the basis of $d_{(110)}$ or $d_{(210)}$ has great potential for being in error.

TABLE 1

Amphibole JCPDS Card No's., $d_{(110)}$ or $d_{(210)}$ Peak Position, and Relative Intensity

JCPDS Card #	Å	2θ (Cu)	I	JCPDS Card #	Å	2θ (Cu)	I
23-118	8.58	10.31	100	20-1390	8.40	10.53	90
10-456	8.55	10.35	100	23-302	8.40	10.53	100
20-734	8.53	10.37	70	19-1063	8.39	10.54	70
20-378	8.52	10.38	100	13-437	8.38	10.56	100
14-633	8.51	10.39	70	17-478	8.38	10.56	65
21-149	8.51	10.39	55	23-495	8.38	10.56	80
19-467	8.50	10.41	100	9-330	8.37	10.57	100
20-982	8.50	10.41	65	17-750	8.36	10.58	25
23-665	8.48	10.43	45	20-386	8.35	10.59	40
23-664	8.47	10.44	35	22-531	8.35	10.59	30
23-667	8.47	10.44	45	16-401	8.33	10.62	70
23-663	8.46	10.46	40	17-725	8.33	10.62	100
9-434	8.45	10.47	50	17-745	8.33	10.62	100
13-499	8.45	10.47	100	20-376	8.31	10.65	100
20-656	8.45	10.47	100	17-726	8.30	10.66	100
20-470	8.44	10.48	100	20-484	8.29	10.67	100
23-666	8.44	10.48	40	13-506	8.27	10.70	80
20-469	8.43	10.49	100	23-679	8.27	10.70	90
23-1405	8.43	10.49	80	9-455	8.26	10.71	55
23-1406	8.43	10.49	40	20-453	8.26	10.71	100
10-428	8.42	10.51	100	11-253	8.23	10.75	100
23-603	8.42	10.51	100	20-1310	8.20	10.79	75
10-431	8.41	10.52	80	23-310	8.20	10.79	75
19-1061	8.40	10.53	100	13-401	8.11	10.91	100
20-481	8.40	10.53	100				

Maximum Δ 2θ (Cu) = 10.91° - 10.31° = 0.6°

Problems further affecting the reliability of amphibole identification are the effects of shift in peak position caused by mispositioning of the sample surface, and method of interpretation of the peak position, e.g., centroid or maxima. The overall significance of $d_{(110)}/d_{(210)}$ peak

position is that it can be used to do no more than to generally eliminate certain amphiboles from further consideration as being present.

Single Peak Identification

Implicit in the preceding discussion is the potential hazard associated with identification of a phase on the basis of a single diffraction peak. An example of erroneous single peak identifications is presented in a paper by Snider, et. al., 1972. Of 18 commercial talcum powders examined by these authors, they reported the XRD identification of anhydrite in 15, serpentine in 13, "clay" in 17, tremolite-actinolite in 9, and anthophyllite in 6. Chlorite, one of the most common accessory minerals found associated with talc was not identified in any of the samples, although their "clay" may in fact be chlorite.

We have examined some of the identical samples reported on by Snider, et. al., and cannot agree with their interpretations of anhydrite, serpentine, and tremolite-actinolite-anthophyllite. We can only conclude that the erroneous identifications presented by Snider, et. al., were made on the basis of single diffraction peaks without any real consideration of potential errors in their identifications.

Abnormal Crystal Habit

In a detailed examination of a commercial talc sample, a minute amount of acicular mineral which appeared to be amphibole was isolated. However, subsequent detailed examination by Gandolfi XRD of five hand-picked grains (all <150 μm long) identified talc without evidence of any amphibole being present. Careful optical examination in oil immersion

media with determination of indices of refraction and extinction angles confirmed the XRD identification of talc as being correct.

X-ray diffraction examination of a different sample of industrial bulk acicular talc revealed the presence of significant amphibole, probably tremolite. Careful optical examination of this sample showed it to be composed of free grains of acicular talc and columnar amphibole, and composite talc-amphibole grains. The talc appears to be pseudomorphic after amphibole, and its unusual acicular habit is likely derived from its amphibole pseudomorph. This occurrence shows an important pitfall where one mineral (talc) can be misidentified as a different mineral (tremolite), and cause the wrong conclusion to be drawn.

INTERFERENCE ERRORS

Serpentine-Chlorite

It is well known that chlorite and serpentine are difficult to differentiate by all known methods of characterization. Generally, however, the (004) XRD peaks are separate enough to allow unambiguous identification of both phases when present in amounts sufficient to give definable peaks. Serpentine and chlorite XRD patterns are usually characterized by broad peaks which are often poorly defined and resolved, especially when present in minor amount.

A situation somewhat similar to that for amphiboles exists for serpentine and chlorites, e.g., similar crystal structure and wide variation in chemical composition. As a result, the diagnostic chlorite (004) peak and serpentine (004), (00$\underline{12}$), or (002) peak shows considerable variation in the position in which it occurs (Tables 2 and 3). The observed

TABLE 2

Chlorite JCPDS Card No's., d(004) Peak Positions, and Relative Intensity

JCPDS Card #	Å	2θ(Cu)	I	Name
10-183	3.60	24.73	100	penninite
20-671	3.60	24.73*	90	kämmererite
16-351	3.59	24.80	70	chlorite 1b
12-185	3.57	24.94	85	kotschubeite
7-160	3.58	24.87	60	kotschubeite
19-749	3.56	25.01	80	clinochlore
7-77	3.558	25.03	50	sheridanite
16-362	3.55	25.08	80	chlorite 1a
19-751	3.55	25.08	65	sudoite
22-712	3.55	25.08	45	nimite
7-165	3.545	25.12	60	grochauite
7-78	3.541	25.15	60	thuringite
7-171	3.541	25.15	80	diabantite
12-242	3.54	25.16	100	leuchtenbergite
7-76	3.537	25.18	50	ripidolite
13-29	3.53	25.23	80	thuringite
7-166	3.523	25.28	50	daphnite
12-243	3.52	25.30	92	aphrosiderite
21-1227	3.52	25.30	100	thuringite
3-67	3.49	25.52	100	thuringite

*d(115)

wide variation in peak positions shown in Tables 2 and 3 demonstrates the need for every sample to be considered on an individual basis. The selection of peaks at 3.65Å and 3.55Å as definitive of serpentine and chlorite respectively can certainly result in erroneous identifications.

Chlorite is a very common accessory mineral associated with talc, whereas serpentine is much less common. When serpentine is present, it typically is at a much lower concentration level than chlorite. Quantification of minor to trace serpentine in the presence of at least equivalent amounts of chlorite is an extremely difficult if not impossible

TABLE 3

Serpentine, Kaolinite, Halloysite, and Dickite
JCPDS Card No's., Peak Position, Miller Index (hkl),
and Relative Intensity

JCPDS Card #	Å	2θ (Cu)	I	(hkl)	Serpentines
18-779	3.67	24.25	80	(002)	lizardite, 1M
9-444	3.66	24.32	100	(0012)	antigorite, 60
21-543	3.65	24.39	70	(004)	chrysotile, 2M
7-417	3.63	24.52	300	(102)	antigorite, 6M
11-386	3.62	24.59	60	(002)	lizardite, 10, aluminan
21-963	3.61	24.66	80	(002)	antigorite, 6M
12-583	3.56	25.01	80	(0012)	antigorite, 60, aluminan
13-4	3.56	25.01	70	(0012)	antigorite, 60, aluminan
7-339	3.55	25.08	100	(002)	berthierine
11-388	3.55	25.08	100	(0012)	antigorite, 60, syn
7-315	3.52	25.30	100	(002)	berthierine
9-493	3.52	25.30	100	(004)	amesite
					Kaolinites
6-221	3.58	24.87	100+	(002)	kaolinite, 1Md
14-164	3.579	24.88	80	(002)	kaolinite, 1T
12-447	3.56	25.01	50	(002)	kaolinite, 1T
					Halloysite
9-453	3.63	24.52	90	(002)	halloysite, dehydrated
					Dickite
10-446	3.58	24.87	100+	(004)	dickite $2M_1$

Chlorite 2θ Range: 24.73 - 25.52

task. Stanley and Norwood, 1973, for example, state that chlorite must be absent in order to quantify low-level serpentine by XRD.

An example of erroneous identification and quantification of serpentine in talc occurred in 1972, where 2.9% serpentine was identified in a talc sample on the basis of two XRD peaks at 12.28° 2θ (7.21Å) and 12.05° 2θ (7.34Å), misinterpreted as chlorite and serpentine, respectively. In contrast, our examination of this sample (Caneer, W. T., 1977) identified

peaks at 7.1Å and 7.22Å. Examination of the 14Å region identified first-order equivalents of these peaks at 14.1Å and 14.47Å, respectively. Examination of the 3.5Å region identified fourth-order equivalent peaks at 3.54Å and 3.61Å, respectively. Since serpentine does not have a 14Å peak, the double peaks in the regions of 14Å, 7Å, and 3.5Å are almost surely due to two chlorites, possibly thuringite and penninite, rather than chlorite and serpentine.

If any of the three clay minerals kaolinite, halloysite, or dickite are present, they will interfere in the same way as does chlorite. Distinction between serpentine and kaolinite, halloysite, or dickite is extremely difficult, however, since unlike chlorite these minerals do not have a peak in the 14Å region that clearly distinguishes them from serpentine. The data of Table 3 shows the severe nature of interference with serpentine of the kaolinite, halloysite, dickite (002) or (004) peaks.

Talc-Quartz

Quartz is often found as a low-level accessory mineral occurring with talc. Identification and quantification of quartz by XRD is a relatively straightforward analysis, but problems do exist. For example, Rohl, et. al., 1976, analyzed a number of talcums for quartz by XRD using the relatively weak (211) quartz peak (I = 15) at 1.54Å (60.08° 2θ for CuKα). However, the strong (060) talc peak (I = 55) at 1.53Å (60.51° 2θ for CuKα) will overlap and mask the presence of small amounts of quartz. Trace to minor amounts of quartz in the presence of major talc clearly cannot be quantified on the basis of $d_{(211)}$ intensity. We suggest that $d_{(101)}$, the

most intense quartz peak, is generally free from interference and is best used for identification and quantification of quartz (CFTA Method J 6-1).

METHODS FOR ELIMINATION OF INTERFERENCE AND INTERPRETATION PROBLEMS

Simple awareness of interpretation and specific interference errors is often effective in prevention of their occurrence. However, solution of the problems surely requires more than to simply know of their existence. Specifically, we have applied techniques involving separation and isolation of the phases of interest, followed by standard and special XRD techniques and confirmatory optical microscopy and microprobe analysis, as required.

Handpicking

A very effective method of isolating minerals for analysis is that of handpicking. The optical microscope is an extremely sensitive analytical tool, capable of detecting impurities at a very low level. However, optical identification of a detected impurity can be difficult, and handpicking for XRD identification is a possible confirming method. The identification of acicular talc described earlier was performed in this manner, e.g., detection by optical microscopy, followed by handpicking, Gandolfi XRD, and finally determination of confirming optical properties.

The Gandolfi XRD method has a number of advantages, as follows:

(1) A powder pattern will be produced from a single crystal as small as about 30 μm.

(2) The sample is not crushed, and thus is available for examination by optical microscopy or microprobe.

(3) The sample is normally composed of only one phase, whereas larger samples increase the chance for introduction of additional phases.

(4) The diffraction pattern obtained is usually very sharp. This is due to the very small sample size and the lack of line broadening from grinding deformation.

Density Gradient Column Heavy Liquid Separation

The density gradient column is an apparatus that can produce very delicate specific gravity separations (Muller and Burton, 1965; Smale, 1970). The method operates by introducing a sample into a column of liquid that is continuously variable in specific gravity; high specific gravity at the bottom to low specific gravity at the top. The components of the sample settle to the level of their specific gravity, and are removed by the extraction apparatus. The method has the ability to separate two minerals having a difference in specific gravity as small as 0.003. For example, we have separated a chloritic talc powder into three fractions by this method. XRD and optical examination of the fractions indicated that the fractions were talc, chlorite, and locked talc plus chlorite.

SUMMARY

In summary, we have discussed specific interpretation and interference pitfalls commonly encountered in the routine examination of talc powders. These included: The inability to identify amphibole species on the basis of $d_{(110)}$ or $d_{(210)}$; chlorite-serpentine and talc-quartz interferences; identifications based on one peak; and talc with amphibole morphology, e.g., amphibole pseudomorphs.

Isolation of mineral species by handpicking and density gradient separation have been suggested as aids in reducing some interference and interpretation problems. Gandolfi XRD and optical microscopy were presented as sensitive analytical methods.

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