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## Computer-Aided X-Ray Diffraction Identification of Crystalline Mixtures in Forensic Science Investigations

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**ABSTRACT:** X-ray diffraction analysis of multiphase mixtures is sometimes rather painstaking and time-consuming by conventional manual identification using search manuals and the Joint Committee on Powder Diffraction Standards (JCPDS) file. This is the reason why a search match program has been developed in FORTRAN IV using a 32 kB Data General Nova 3/12 minicomputer with floppy disk storage to evaluate X-ray diffraction patterns in an on-line mode, regardless of intensities, permitting the mixture components to be determined from a compiled data file of forensically relevant substances. This paper discusses the problems of procedure, program setup, and results.

**KEYWORDS:** forensic science, X-ray analyses, crystalline material, computers, search match program

Forensic science applies X-ray diffraction analysis to the investigation of explosives, paint flakes, raw and building materials, minerals, accelerant and extinguishing agents, general traces on exhibits, and, to some extent, the identification of organic crystalline substances and drugs.

The physical basis of this process is the interaction between X-rays and the periodically arranged atomic particles of crystalline substances. The vast majority of inorganic solids—except glass—as well as many organic substances follow this structural principle by interlinking their atoms, molecules, or ions into lattice planes and space lattices, which gives the substance a specific crystal structure.

X-ray diffraction of crystal powders by the Guinier, Debye, or diffractometer methods easily enables the interplanar  $d$  spacings of lattice planes to be calculated using Bragg's equation  $n \cdot \lambda = 2d \cdot \sin \theta$ . From the wavelength  $\lambda$  of the X-rays used and the registered diffraction angles  $\theta$ , it is possible to perform an identification by comparison with the spectra of known substances. Although there is no problem to identify pure substances by means of the Joint Committee on Powder Diffraction Standards (JCPDS) file which currently includes about 30 000 spectra, it is somewhat more difficult to evaluate diffraction spectra of mixed crystals because of the systematic shifting of  $d$  values caused by substitution of particles. Some well known examples are given by the materials brass (copper-zinc alloy) and argentan (copper-nickel-zinc alloy) used for coinage and falsification of coins. These phases are rarely

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included in the JCPDS file and the numerical data of their powder diffraction patterns must either be prepared anew or be derived from specific literature.

A more complex task is the analysis of multiphase materials because the number of possible  $d$  value combinations leading to an identification of individual phases may become large. As an aggravating fact, it should be considered that the number of diffraction lines of a compound recorded depends on its percentage contained in the mixture. Furthermore coincidence occurs for identical  $d$  values of different constituents in a multiphase system.

In addition to these problems encountered in mixture analysis in general, there are other factors of influence. These are a result of the properties of materials examined in forensic science work, which shift the analysis procedure sometimes towards the boundaries of applicability. Preparatory restrictions, material composition, and small quantities of these substances counteract the adjustment of optimum recording conditions and thus the quality assurance for a reliable mixture identification.

Of all applicable X-ray diffraction methods, the Forensic Science Institute of the Bundeskriminalamt prefers the Guinier technique because of its superiority to the mentioned methods in the criteria of resolving power, precision, substance amount needed, and detection sensitivity. Figure 1 shows the X-ray diffraction spectrum of a homemade explosive from an 1982 case, as an example.

To recognize significant secondary compounds of a mixture, our Guinier films often have to be overexposed so that the important identification criterion—intensity of diffraction lines—can hardly be used by the search match routine. These conditions had to be faced for the computer-aided evaluation of X-ray diffraction patterns.

### Conception

Since the identification of all substances within a mixture may well take several hours by manual evaluation, computer programs were developed some years ago for large-scale computer systems, permitting the identification of substances by means of the JCPDS magnetic tape file. Detailed test runs performed by us in the years 1975 to 1976 based on a search match program developed by Johnson and Vand [1] did not yield any satisfying results under the aggravated conditions mentioned above.

The hardware side of our X-ray laboratory equipment were new Enraf-Nonius Guinier cameras, an optical device with analog digital converter for the film evaluation and an interface to the Nova 3 minicomputer. These were considered the basic requirements for a computer-aided identification of substances, such that the remaining solution should be found in conjunction with a suitable identification strategy. Owing to the low storage capacity of the computer the programs were written in FORTRAN IV.

### Program for Calculating the $d$ Values

For the correction of measuring results and exact calculation of interplanar spacings, it is necessary to mix the sample with a calibration standard. However, for the sake of keeping the exhibits clean for continued analytical examinations, this is not desirable in most cases since it induces additional diffraction lines into the pattern of the mixture.

Nonetheless, calibration is necessary for accurate measuring and calculation of lattice



FIG. 1—Guinier X-ray pattern of a homemade explosive.

constants. Therefore, various program modifications have been prepared which, on one hand, provide prior determination of camera corrective factors by the least squares method using silicon standard patterns and, on the other hand, permit an up-to-date correction of measuring errors on sample calibration-standard mixtures.

The measured values can be either transferred directly from an optical measuring device by the program or entered manually via the console. After calculation, a list of interplanar spacings is issued and a disk file "Angles 2-Theta" is produced and the 2-theta data calculated is used for the subsequent search match programs.

### X-Ray Diffraction File of Forensically Relevant Substances

A summary of evaluation results from 2000 patterns taken in the period between 1976 and 1981 led to an inventory of 220 inorganic substances, identifiable either individually or in mixtures of 2 to 6 compounds. This represents the basis of our own X-ray diffraction file. As the file is to be updated continuously, its expansion has been provided in a subroutine of the search match program. Its setup is illustrated in Table 1.

Each substance line starts with a serial file number, the JCPDS file number, and the name or formula of the substance, followed by characteristic elements or polyatomic groups, as well as an evaluation vector (EVA), determining in three steps the minimum number of coinciding measurement and data values required for the output of each substance. The sequence of EVA numerals is determined by the total number of diffraction lines in the recorded angular area and by the number of lines with high intensity. Each substance line is completed by the input of eight  $d$  values with decreasing intensity, which are converted into angular values  $2\theta$  for the wavelength  $\text{Cu K } \alpha_1 = 0.15405 \text{ nm}$  by the program according to Bragg's equation and stored as a four-digit integer. If a substance includes less than eight lines in the recorded range, the line will be completed by zeroes.

### Identification Program

The development of minicomputer programs to solve X-ray diffraction identification problems started from the demand for an intensity criterion [2-6]. Even if we have to waive line intensities, as mentioned already, the measured  $d$  or  $2\theta$  values and possible chemical preset values for existing elements or polyatomic groups will be available as input data. Therefore the identification problem can be presented as a straightforward mathematical operation.

A vector **NZTG** with  $N$  elements, corresponding to the corrected measured values of the X-ray diffraction diagram, and a matrix **NZT** of  $(I, J)$  elements, according to the number  $I$  of substances and  $J$  of 2-theta file data, is given. The elements of matrix **NZT** included in the vector **NZTG** must be determined.

Without any chemical presets and within the relatively small data matrix of  $220 \cdot 8 = 1760$  elements, the computer has to perform about 140 000 numerical comparisons for identification of a mixture whose diffraction diagram exhibits 80 lines.

Furthermore the algorithm has to include criteria for the solution of the identification problem.

TABLE 1—Setup of disk file data.

No.	JCPDS-No.	Name	Elements	EVA	2-Theta Integers ( $\cdot 100$ )								
0089	5.0628	NaCl	Na	Cl	346	3169	4544	5647	2735	5384	6622	7529	0000
0105	14.0544	KClO <sub>3</sub>	K	Cl	358	2580	2666	3115	2011	3200	3218	3865	4271
0106	7.0211	KClO <sub>4</sub>	K	Cl	358	2552	2835	3091	1984	2450	2651	3156	4164
0107	5.0610	NaClO <sub>3</sub>	Na	Cl	357	3036	2708	5200	1906	2340	3334	4114	4571

The elements of the vector **NZTG** are physical quantities to be measured and as such may be afflicted with errors. The margin of error most likely is linked to the vector elements.

The EVA vectors are assigned to a  $(220 \cdot 3)$  elements matrix whose columns can be called by the user of the program.

The respective  $d$  and  $2\theta$  values of the file substances are ordered with decreasing intensity and the two values corresponding to the highest intensity reflections are to be marked for identification.

If chemical elements or polyatomic groups are specified, only the substances of the file containing at least one of these elements will be included in the search match procedure. These results lead to the program flow chart illustrated in Fig. 2.

The program starts with reading in of the disk files Data and Angles 2-Theta and covers the identification criteria to be determined by the user in the dialog mode (Table 2).

The margin of error  $\Delta 2\theta$  is decisive for the allocation of measured and data values, by the comparison  $2\theta_{\text{meas.}} - 2\theta_{\text{data}} \leq \Delta 2\theta$ . In a positive case, both the data and the measured values are marked by an asterisk (\*), and the number of markings per substance are counted.

The evaluation Step 1, 2, or 3 controls the column of the EVA-matrix in the file. For instance, in Column 1 it interrogates whether the number of \* markings of a particular substance is equal to the first digit of the corresponding vector. Increasing the evaluation step to 3 demands the greatest number of conforming measured and data values. Depending upon the total number of lines of a compound in the registered area, this means about three to eight marked  $d$  values.

Using the search match criterion  $NVOR = 1$ , one can determine whether the two lines of highest intensity within a substance must be marked or whether the asterisks may be distributed randomly. In the negative case it is possible to identify substances in overexposed X-ray patterns by the strongly widened lines of high intensity, despite any major measuring errors.

As an additional decision aid, the elements or polyatomic groups known from other analysis methods can be entered. Then the program will perform its comparison only with the data sets of those combinations meeting at least one of the chemical requirements. This makes identification more reliable, particularly for X-ray patterns including many lines.

The search routine consists of several nested loops (refer to Fig. 2). Firstly, chemical data of the sample, if any, are compared to the elements of the individual file substance. This is followed by a comparison of all measured values with the  $2\theta$  data file values of the substance just checked. All coinciding figures are marked, the number of markings is counted and checked whether this value is equal to or higher than the digit of the EVA vector of this substance, selected via the evaluation step.

Whenever the request for the search match criterion is answered by 1, it still has to be checked whether the two lines of highest intensity have been marked.

Upon fulfillment of all criteria, the substance is regarded as identified and delivered as an output, together with the applicable JCPDS file number and the  $d$  values matched and marked. This is followed by a branch to the beginning of the nested loops and the start of the same test routines for the next file substance. Having worked through the complete file by this procedure and having prepared a proposal list of substances in the mixture investigated, the user may terminate the program or have a new proposal list prepared using altered search parameters.

Computer identification (Table 2) of the homemade explosive showed after measurement of 80 lines under obvious criteria a complete list of mixture compounds, because all lines shown in the X-ray diffraction pattern could be assigned to the substances sodium chloride, sodium chlorate, potassium chlorate, and potassium perchlorate.

## Conclusion

The functions of the search match program were reviewed by means of several tests with mixtures of known composition. For about one year, the programs have been used for daily

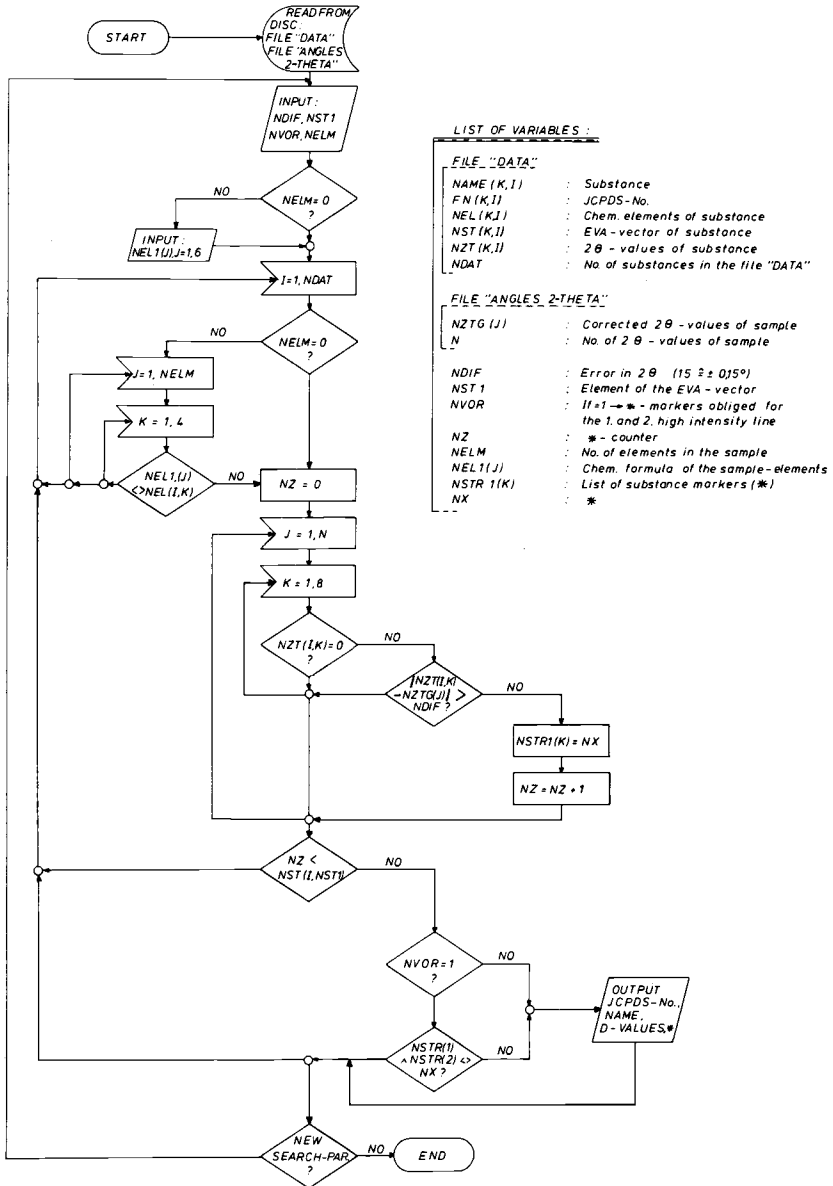


FIG. 2—Algorithm for search routine.

TABLE 2—Identification of the X-ray diffraction pattern homemade explosive.

List of Values											
No.	2 $\theta$	d	No.	2 $\theta$	d	No.	2 $\theta$	d	No.	2 $\theta$	d
01	13.17	6.717	21	31.66	2.824	41	43.40	2.083	61	55.77	1.647
02	15.68	5.647	22	31.92	2.801	42	43.64	2.072	62	56.39	1.630
03	19.01	4.664	23	32.12	2.784	43	45.38	1.997	63	56.88	1.617
04	19.81	4.478	24	33.27	2.691	44	45.65	1.986	64	57.06	1.613
05	20.05	4.425	25	34.67	2.585	45	47.26	1.922	65	57.41	1.604
06	20.63	4.304	26	35.39	2.534	46	47.78	1.902	66	57.65	1.598
07	23.36	3.805	27	35.60	2.520	47	48.55	1.874	67	58.13	1.586
08	23.48	3.766	28	38.07	2.362	48	49.90	1.826	68	58.55	1.575
09	24.48	3.633	29	38.59	2.331	49	50.17	1.817	69	59.07	1.563
10	25.46	3.495	30	38.90	2.313	50	50.59	1.803	70	59.47	1.553
11	25.70	3.463	31	39.28	2.292	51	50.92	1.792	71	61.35	1.510
12	26.59	3.349	32	39.67	2.270	52	51.21	1.782	72	61.85	1.499
13	27.02	3.297	33	41.06	2.196	53	51.91	1.760	73	62.17	1.492
14	27.28	3.266	34	41.60	2.169	54	52.37	1.746	74	62.42	1.486
15	27.50	3.241	35	41.76	2.161	55	52.63	1.738	75	63.07	1.473
16	27.76	3.211	36	41.91	2.154	56	53.28	1.718	76	64.85	1.437
17	28.32	3.149	37	42.02	2.148	57	53.76	1.704	77	65.10	1.432
18	30.33	2.944	38	42.26	2.137	58	53.96	1.698	78	65.50	1.424
19	30.90	2.891	39	42.64	2.119	59	54.19	1.691	79	66.13	1.412
20	31.09	2.874	40	42.81	2.111	60	54.51	1.682	80	66.59	1.403

## SEARCH-MATCH PROGRAM

Film no. : 7201  
 Angle input floppy disk (1) or manual (2) : 1  
 Margin of error ( $\Delta$ -2-Theta) : .15  
 EVA-Vector Column (1, 2 or 3) : 3  
 Search match criterion NVOR = (1) or (2) : 1  
 No. of known elements in the sample : 0

JCPDS-No.	Name	d Values Matched*									
5.0628	NACL	2.821*	1.994*	1.628*	3.258*	1.701*	1.410*	1.261	0.000		
14.0544	KCLO3	3.450*	3.341*	2.869*	4.412*	2.794*	2.779*	2.328*	2.115*		
7.0211	KCLO4	3.487*	3.145*	2.890*	4.471*	3.630*	3.359*	2.832*	2.167*		
5.0610	NACLO3	2.942*	3.290*	1.757*	4.652*	3.798*	2.685*	2.192*	1.983*		
		New search parameters (1) or stop (0) : 0									
		Stop									

routine investigations and have proved very useful as an aid to identification. Although in individual cases the multiphase mixtures can not be recognized completely, there lies a certain improvement and facilitation for the subsequent manual identification of the phases not recognized.

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