

ON SOME DISTRACTING BEHAVIOUR OF AUTOMATIC X-RAY DIFFRACTOMETER

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Two distracting situations have been discussed which were faced while working with the automatic X-ray diffractometer, Siemens D-5000. These problems, appeared to be, in one case, the result of the climatic conditions and working environments in the laboratories, whereas the second one was found to arise due to the special impurity emitted by the X-ray tube.

Key words: X-ray diffractometer, Scintillation counters, Spectral impurity.

Introduction

The commercial computer controlled powder diffractometers with the scintillation counters using pulse-height discrimination and the step-by step-method of recording are very common these days. The sources of instrumental errors like the transparency of the specimen to X-radiation, the displacement of the specimen from the axis of rotation, the Lorentz, polarization and dispersion factors (Cullity 1978) are also well known and have been discussed by several authors (Klug and Alexander 1974; Jenkins 1983; Parrish and Huang 1983). Yet, it has been a usual practice that even with a well aligned instrument there are some unindexed peaks left in the diffraction patterns of pure single phase specimen often referred as ghost/false peaks (Synder 1983; Huang *et al* 1984).

Two baffling problems arose while working with the computer controlled X-ray diffractometer Siemens D-5000. On close examination of these problems i.e. (i) the occurrence of extra diffraction lines and (ii) the misbehaviour of scintillation counter, it was found that the occurrence of the extra lines were other than the ghost/false peaks reported in the literature. The other problem appeared to be the result of the climatic conditions and working environments, as we have in our laboratories, which is rather typical of the tropical climate at its worst during hot and humid summer. We feel that our experiences with these problems may be relevant and beneficial to the X-ray diffractionists working in similar environments.

Description of the Problems. Computer controlled X-ray diffractometer, Siemens D-5000, was installed in 1990 in the PCSIR laboratories at Karachi. In the early stages, the diffraction patterns obtained were quite consistent. The pattern obtained with standard samples were in excellent agreement

with standard data. After two years, there started appearing unexplained peaks even with relatively pure samples. Any attempt to explain them to correspond to some extra phase did not work. One hardly suspected them to come from spectral impurity. The persistent appearance of these extra peaks made it necessary to look at them more critically. The problem was communicated to the manufacture of the X-ray diffractometer D-5000 and having no reply from them, Trials were made and eventually the problem was successfully sorted out.

In the case of quartz, it was seen that odd peaks at 2.66 and 2.93 Å^o appeared even on standard quartz pattern taken with copper tube; back tracing their appearance in patterns taken earlier, it was observed that the intensities of these extra peaks got progressively stronger with the passage of time, so much so that most of the extra peaks started persistently appearing as these peaks became sufficiently stronger in intensity. A little effort showed that these extra peaks had some definite relationship with the strong peaks of the pattern; corresponding to each strong peak of the pattern, there appeared two extra peaks. Figure 1 shows the quartz pattern taken at the time of installation, alongwith the patterns taken at later stages, which clearly indicate how these extra peaks were getting stronger with time. Figures 2 and 3 show similar phenomenon with potassium bromide and zinc oxide standard samples. As only one X-ray tube (copper target) had been supplied with the instrument, there was no way to check this phenomenon with another tube. Assuming that the extra peaks were the result of some sort of spectral impurity emitted by the X-ray tube, the wavelength responsible for these extra peaks could be worked out. As the d-value (d₂) for the extra peaks were calculated on the assumption that they were caused by CuK α radiation (λ_1), the relationship for calculating the actual wavelength (λ_2) causing the extra peaks could be worked out using the following formula;

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$$\lambda_2 = \frac{d_1}{d_2} \lambda_1$$

d_2 is the d-value calculated for the actual d1 peak of the pattern, obtained with $\text{CuK}\alpha$ radiation (λ_1), λ_2 is the wavelength for the odd line

Using this relationship, the wavelength values for the pair of extra peaks for only the intense lines of each pattern have been worked out (Table 1) for the different patterns (Figs 1-3). λ_2 values calculated in each case are remarkably consistent (Table 1). These peaks are, in fact, Fe $\text{K}\alpha$ and Fe $\text{K}\beta$ lines which are extra lines due to spectral impurity checked later on by using another copper tube that was made available.

The other problem was associated with the detector. The instrument is equipped with scintillation counter as radiation detector. While collecting diffraction data with this system, the count rate was found to shoot up inordinately and this did not drop down even with the decrease in the X-ray generator ratings, and it appeared that the counter had got saturated. Hence no data collection was possible. The unit thus had to be switched off; and after waiting for the counter to come to normal (it takes some hours), efforts were made to start the data collection again, but it was observed that within minutes, the count rate again shot up inordinately. This problem was luckily sorted out as arising due to high temperature and

humidity in those working days, for which no adequate protection had been taken. This problem was resolved by airconditioning the X-ray room and putting a bag of silica gel in the enclosure housing the X-ray tube and the

Table 1

Identification of the origin of the extra lines

Genuine extra peaks	2θ	$\lambda_2 = d_1/d_2 \times \lambda_1$	Origin of extra lines	
<i>Quartz</i>				
3.345	2.937	30.416	1.753	Iron $\text{K}\beta$
	2.662	33.645	1.936	Iron $\text{K}\alpha$
<i>Potassium bromide</i>				
3.300	2.894	30.880	1.757	Iron $\text{K}\beta$
	2.626	34.126	1.937	Iron $\text{K}\alpha$
2.334	2.046	44.246	1.758	Iron $\text{K}\beta$
	1.856	60.575	1.938	Iron $\text{K}\alpha$
<i>Zinc oxide</i>				
2.814	2.465	36.421	1.760	Iron $\text{K}\beta$
	2.240	40.237	1.936	Iron $\text{K}\alpha$
2.603	2.285	39.410	1.756	Iron $\text{K}\beta$
	2.071	43.686	1.937	
2.475	2.172	41.542	1.756	Iron $\text{K}\beta$
	1.970	46.050	1.936	Iron $\text{K}\alpha$

Note: The values of d-spacing, wave lengths and 2θ have been approximated to three decimal places λ_1 (waves length of $\text{Cu K}\alpha_{1+2}$) is taken as 1.541 Å°.

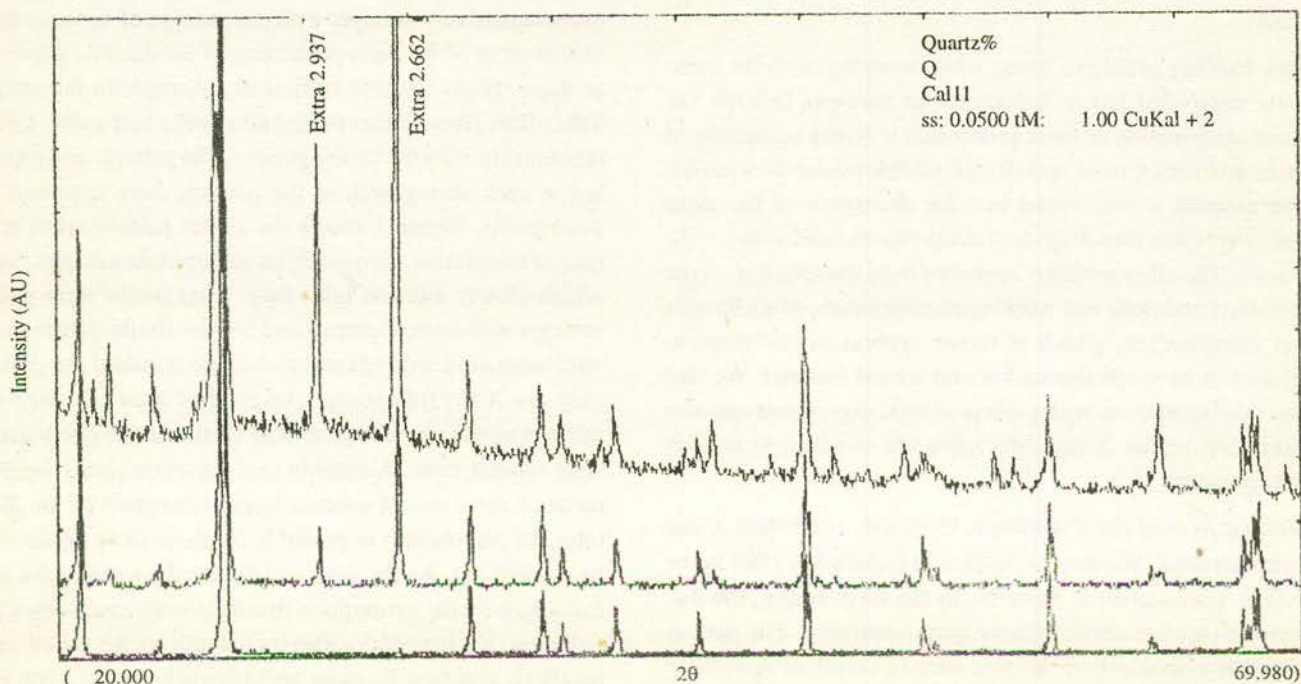


Fig 1. X-Ray powder pattern of quartz taken at the time of installation alongwith patterns taken at later stages.

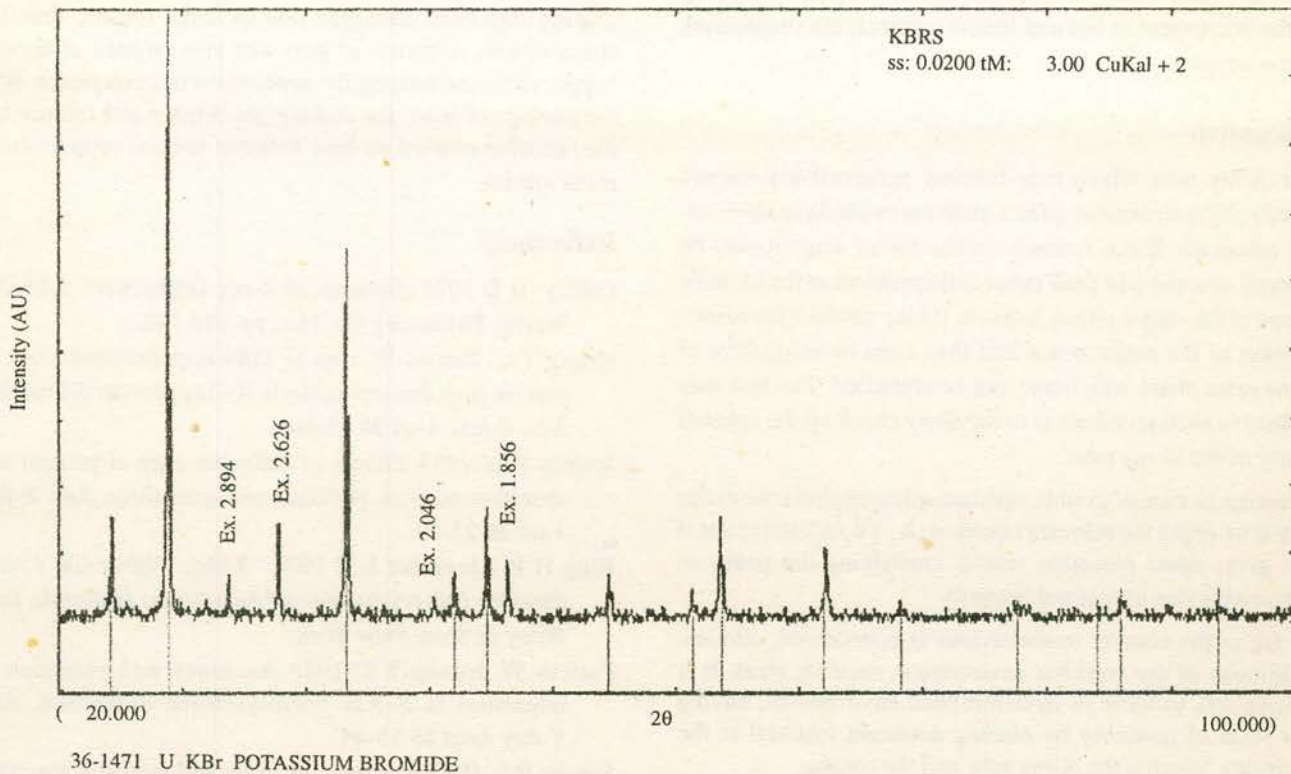


Fig 2. Potassium bromide pattern alongwith its std. data, shown as vertical lines. (JCPDS card No.36-1471).

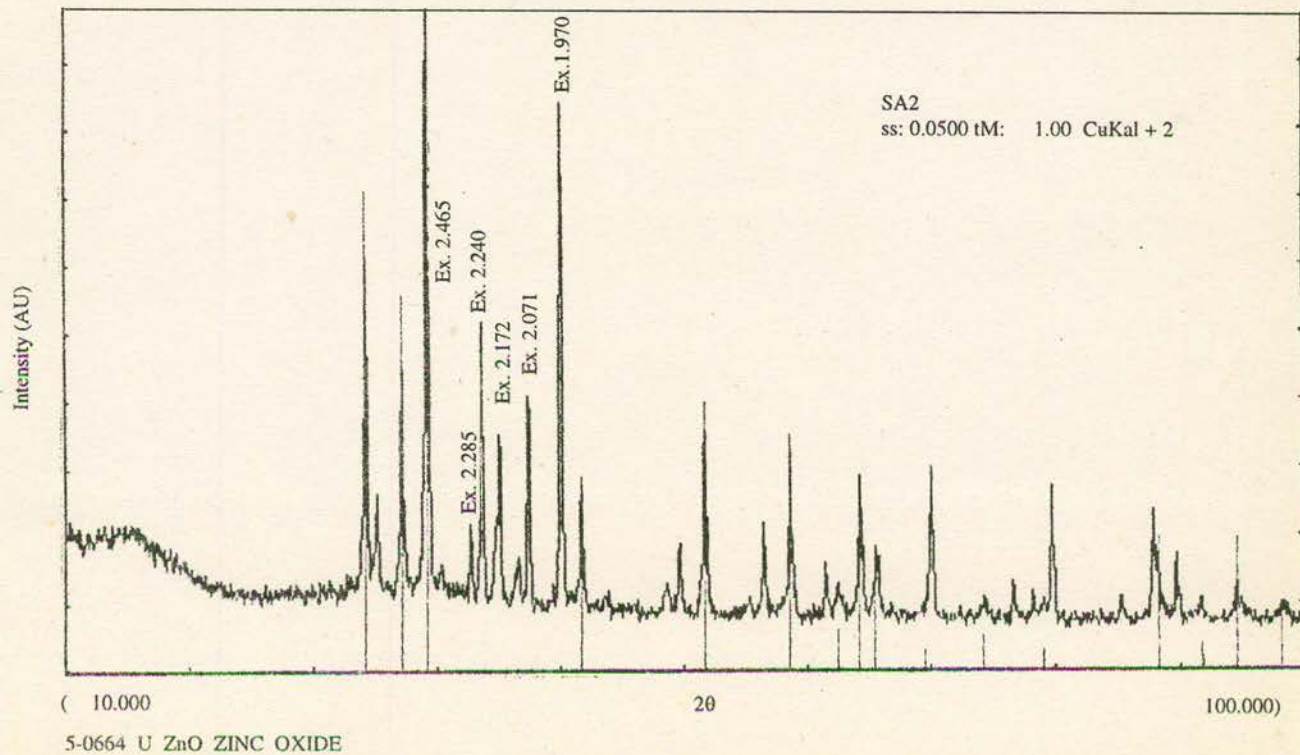


Fig 3. Zinc oxide pattern alongwith its std. data, shown as vertical lines. (JCPDS card No.5-0664).

detector. Thus it was concluded that for the proper working of the instrument in hot and humid summer, airconditioning was necessary.

Discussion

The X-ray tube which may become progressively impure (spectrally) can present quite a problem in phase analysis using automatic X-ray systems. In the earlier stage it may be ignored as some odd peak cause little problem in the identification of the major phase; later on, it may confuse the identification of the major phase and may even be suggestive of some extra phase which may not be identified. The best way to resolve such problems is to regularly check up the spectral purity of the X-ray tube.

However, in case of trouble with unexplained peaks the easier way is to apply the relevant equation ($\lambda_1 \times d_1/d_2$) and to see if this gives some plausible results identifying the peaks as extra peaks due to spectral impurity.

As far as the counter misbehaviour is concerned, climatic conditions of the working environment must be ideal. It is always safe to work in airconditioned environment, having low level of humidity by placing dessicant material in the enclosure housing the X-ray tube and the counter.

The most probable cause of the spectral impurity in our case, was that the anode of the X-ray tube comprising of copper

coating on iron base had become defective. The copper coating had been damaged due to some reason, thus the characteristic radiation of iron was also emitted alongwith copper radiation causing the appearance of extra peaks. With the passage of time, the coating got thinner and thinner and the radiation emitted by base material became progressively more intense.

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