

## QUANTITATIVE X-RAY DIFFRACTION ANALYSIS OF $\alpha$ -PbO/ $\beta$ -PbO IN LEAD-ACID BATTERY PRIMARY OXIDE

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### Summary

The quantitative X-ray powder diffraction technique has been adapted for the analysis of the lead oxide used in the manufacture of lead-acid batteries. Such oxide, containing free lead and two polymorphs of lead oxide ( $\alpha$ -PbO,  $\beta$ -PbO) is the primary component used for the manufacture of positive plate paste in the lead/acid battery. The method described determines quantitatively the  $\alpha$ -PbO and  $\beta$ -PbO crystalline phases using an internal standard technique, thus enabling battery manufacturers to monitor changes in the composition of their oxides with variations in operating conditions of the process.

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### Introduction

The precise effect the lead/lead oxide composition has on the positive plate paste and the subsequent effect this has on the final performance and longevity of the battery has yet to be resolved. Commercially, the oxide composition is not maintained to a strict specification, having been determined by observation and experience. A typical composition using the "Bartøn Pot" method of manufacture would be:

20 - 30% free Pb

5 - 15%  $\beta$ -PbO

60 - 75%  $\alpha$ -PbO

Evidently,  $\alpha$ -PbO is favoured over  $\beta$ -PbO, which, while often considered detrimental to paste quality, is still believed to be a necessary component. Although both are converted to basic lead sulphate, it appears likely that different ratios of the oxide polymorphs lead to different product distributions in the cured positive plate paste owing to (suspected) differing reactivities of the oxides.

Hence, a knowledge of which of the basic sulphate(s) is morphologically and chemically desirable, and any understanding of how the  $\alpha$ -PbO/ $\beta$ -PbO ratio in the primary oxide influences product distribution, will allow some control in obtaining the desirable phase in the cured paste. Several authors have reported the effects of PbO modifications on basic lead sulphate product distribution. Biagetti and Weeks [2] pointed out the differences in polymorph reactivity in sulphuric acid. To produce tetrabasic lead sulphate, it was found that the presence of  $\beta$ -PbO was essential. Under identical reaction conditions,  $\alpha$ -PbO produced a poorly defined mixture of materials. Pavlov *et al.* [3] further substantiated the importance of the presence of  $\beta$ -PbO in the formation of tetrabasic lead sulphate, and that product distribution will vary with mixing time and temperature. Iliev and Pavlov [4] examined the influence of the PbO modifications on the kinetics of the tetrabasic sulphate formation and showed that both were necessary to obtain optimum formation of this phase at 80 °C.

Skoluda *et al.* [5] carried out surface area measurements on positive plates prepared from a variety of commercial oxides. These authors suggested a correlation between  $\beta$ -PbO and BET specific surface area, where the higher the PbO component, the lower the BET specific surface area, due to less PbO<sub>2</sub> being present in the formed plate. Agreement with Burbank's suggestion [1] that anodic oxidation of  $\alpha$ -PbO is easier than that of  $\beta$ -PbO was noted. The effects the  $\alpha$ -PbO- $\beta$ -PbO ratio have on paste (cured and formed) morphology and chemistry requires further investigation, therefore, particularly since there is commercial interest in this ratio.

### Quantitative X-ray analysis

The methodology of quantitative X-ray diffraction (XRD) analysis is well documented [6 - 8]. The method proposed here is one which utilizes an internal standard. Examples of practical application of such methods are those of Hill [9] and Harris *et al.* [10] who carried out quantitative phase analysis on the positive plate of the lead/acid battery.

The theory of the method, briefly, is that the intensity of a diffraction peak from a given phase depends on the concentration of that phase. Intensity and concentration are not, however, linearly dependent, because diffraction intensity depends on the absorption coefficient of the mixture, the value of which also varies with concentration. Hence, by measuring the intensity of a peak from a phase added to the original mixture, and by determining the ratio of the intensities of a peak from the phase of interest to that of the internal standard peak, the non-linear variable in the intensity/concentration function is cancelled.

Thus, for a mixture consisting of a phase, x, and internal standard, s, the following expression can be written:

$$I_x/I_s = K_x W_x$$

where  $I_x$  represents the integrated intensity of a peak from phase x,  $I_s$  the integrated intensity of a peak from phase s,  $K_x$  the constant of proportionality, and  $W_x$  the weight fraction of phase x.

Such an expression depends only on the weight fraction of phase x and a constant weight fraction of s.

There are two possible means of obtaining the proportionality constant  $K_x$ . One is to synthesize mixtures of the phases of interest with a constant weight fraction of the internal standard, obtain the integrated intensities of appropriate peaks and plot intensity ratios for the various peaks *vs.* weight fraction of the appropriate phases. Such calibrations can then be employed for the determination of unknown compositions. A second method relies on a substantial knowledge of the atomic structure of the crystallites, so that the constants may be calculated using the fundamental diffraction equation. Such a method is favoured by Harris *et al.* and Hill because it gives inherently greater reliability by reducing the possibility of error propagation in unknown determinations due to uncertainties in experimentally determined calibration constants.

X-ray diffraction analysis is plagued with practical difficulties which make sample preparation extremely important. Quantitative analysis relies on the morphological consistency of the sample and difficulties in obtaining reproducibility and accuracy occur when factors independent of composition interfere with the composition-dependent parameters which are being measured. Such factors usually come under the headings of preferred orientation, secondary extinction, and micro absorption.

The need for careful and consistent sample preparation cannot be over emphasized. Very careful and thorough grinding of the samples is essential. Where several powder phases are being combined, thorough mixing is also of vital importance to ensure that the X-ray scans a homogeneous sample. Such preparation will help to reduce secondary extinction and micro absorption, although complete removal of preferred orientation can never be conceded and is usually the major reason for large variations in peak intensities. Hill [9] and Harris *et al.* [10] overcame this problem by obtaining the integrated intensities of several peaks from each phase to help average out the effects of preferred orientation. The extent to which such a procedure can be applied depends on the number of suitable peaks, the time available, and the accuracy required. Many peaks may have to be discarded because of lack of resolution and/or amplitude. In this case, an alternative may be to select, say, two peaks from each phase for measurement, scan two random samples from a mixture and average the results obtained.

In selecting a suitable internal standard, the criteria are that it be a crystalline substance with a well defined X-ray pattern, and one which does not severely conflict with peaks of phases to be measured. It is also important that, to obtain measurable peaks, it need not be added in proportions such that measurement of other phases is made difficult.

## Experimental

### *Free lead determination*

This phase need not be determined by XRD since it can be estimated by simple wet chemical analysis. Thus, by adding a known quantity of the leady oxide to hot water, followed by the addition of acetic acid, the free lead was separated. It was then dried and weighed to determine its weight fraction in the mixture.

### *Preparation of pure $\alpha$ -PbO and $\beta$ -PbO phases*

XRD analysis of analytical grade PbO (Pronalys AR, May and Baker) showed it to be a mixture of  $\alpha$ -PbO and  $\beta$ -PbO. Pure  $\beta$ -PbO was obtained by placing 20 g of this mixture in a ceramic crucible which was baked in an electric furnace at 580 - 600 °C [11, 12] for 3 h and then slowly cooled. This process yielded a bright yellow powder which produced a well-defined XRD pattern of  $\beta$ -PbO.

To prepare  $\alpha$ -PbO, 200 cm<sup>3</sup> of 15N NaOH was added to a flask containing 20 mg of  $\beta$ -PbO. After fitting a soda lime tube, the flask was heated to 70 °C and the contents stirred: heating continued for approximately 3 h and was followed by a slow cool to room temperature [11]. The red  $\alpha$ -PbO was filtered, washed with distilled water and vacuum dried. The material thus obtained yielded a well-defined XRD pattern of  $\alpha$ -PbO.

### *X-ray diffraction analyses*

The XRD analyses were carried out on a Rigaku diffractometer fitted with a Philips X-ray tube. Cu K $\alpha$  (35 kV, 25 mA) radiation was used in all experiments and since the samples contained lead which has a high X-ray absorbance, low scanning rates were necessary. A step scanner was thus employed with a scanning rate of 0.002° s<sup>-1</sup>.

Calibration standards were prepared by combining  $\alpha$ -PbO and  $\beta$ -PbO in various proportions with a constant 0.2 weight fraction of the internal standard. After thorough mixing and grinding, these preparations were scanned in the appropriate  $2\theta$  intervals on the XRD unit to obtain calibration lines for  $\alpha$ -PbO and  $\beta$ -PbO at a number of selected diffraction peaks.

## Results and discussion

Figures 1(a) and (b) show the standard XRD patterns obtained for the  $\alpha$ -PbO and  $\beta$ -PbO used in the preparation of the calibration standards. Sodium fluoride was selected as an internal standard. As seen in Fig. 1(c), the most intense peak occurs at 38.8° and is well resolved. A constant weight fraction of 0.2 NaF was found to yield a relatively large peak and at the same time maximise the quantities of the  $\alpha$ -PbO and  $\beta$ -PbO which could be added, thus maximising X-ray sensitivity to these phases.

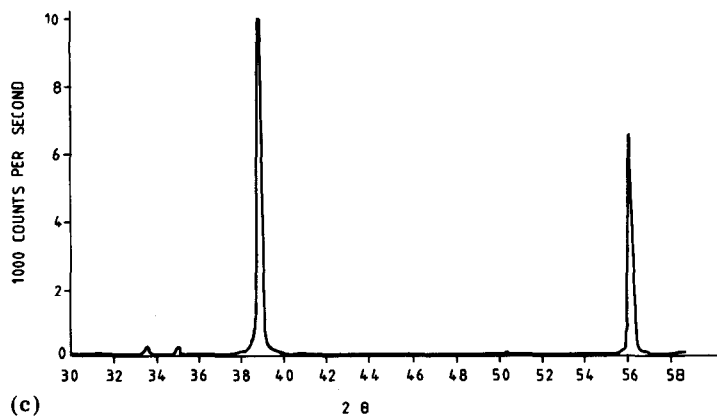
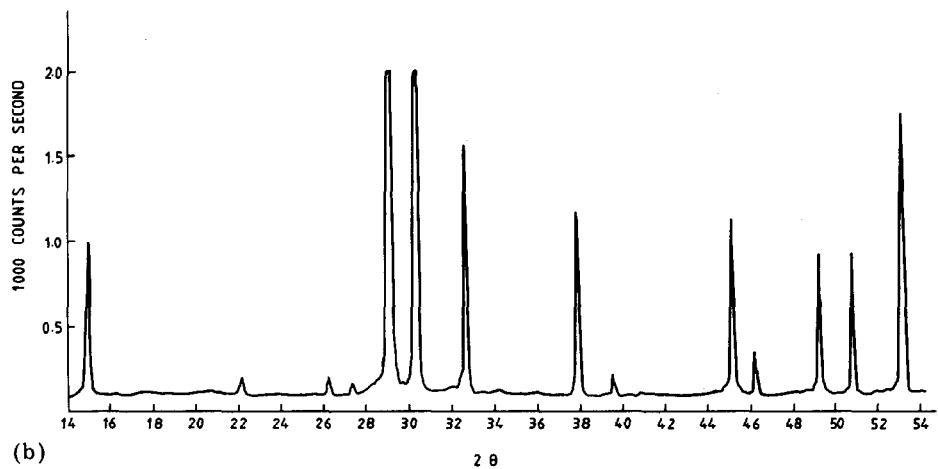
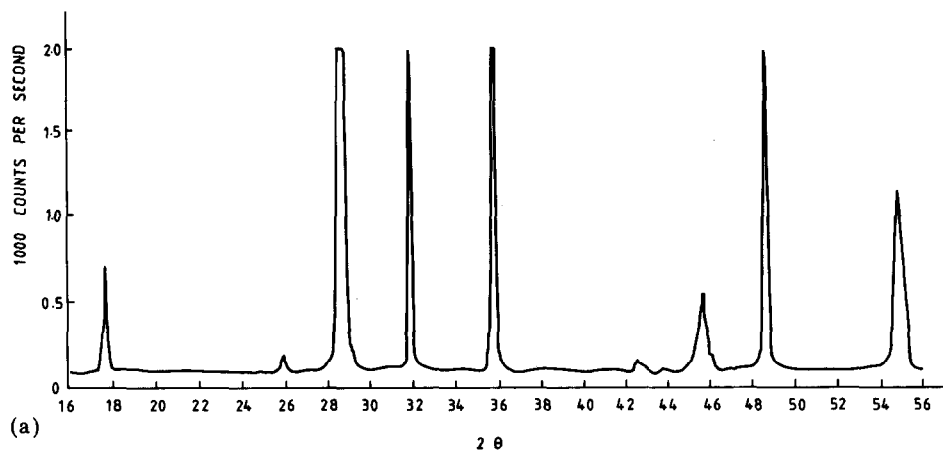


Fig. 1. X-ray diffraction pattern for: (a)  $\alpha$ -PbO; (b)  $\beta$ -PbO; (c) NaF.

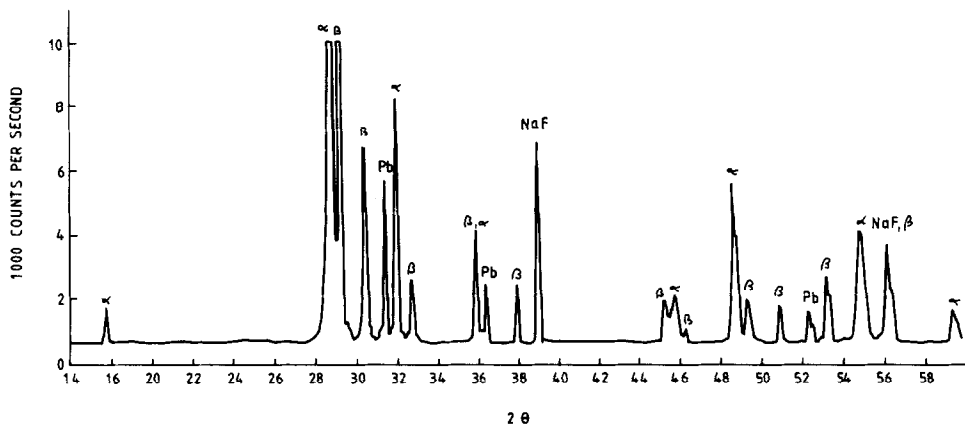
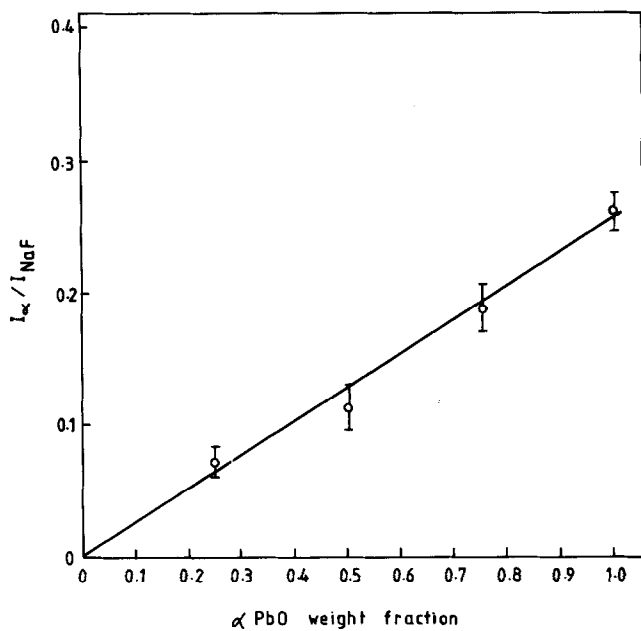


Fig. 2. X-ray diffraction pattern for typical battery oxide and NaF mixture (NaF weight fraction, 0.2).

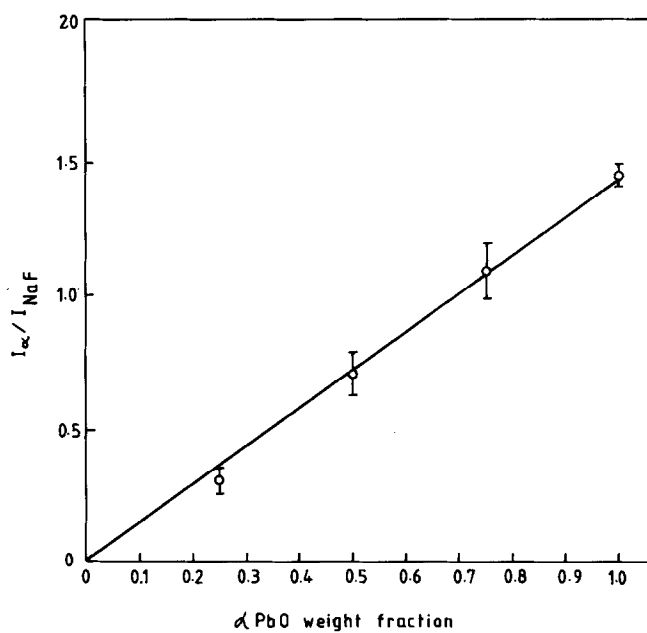
An XRD pattern for a typical battery oxide and internal standard mixture is presented in Fig. 2, relevant  $\alpha$ -PbO,  $\beta$ -PbO, Pb, and NaF peaks being indicated. This shows that most of the measurable peaks occur in a  $2\theta$  range of  $14 - 56^\circ$ . Intensity measurements were thus confined to this region of the diffraction pattern. Very few peaks within this range are, however, useful for intensity measurements in lead/lead oxide mixtures. Unfortunately, the maximum intensity peaks from both  $\alpha$ -PbO and  $\beta$ -PbO at  $28.6^\circ$  and  $29.1^\circ$ , respectively, are unresolved. Another major  $\alpha$ -PbO peak at  $48.6^\circ$  is also in conflict with a small  $\beta$ -PbO peak. Further conflict occurs between major Pb and  $\alpha$ -PbO peaks at  $31.3^\circ$  and  $31.8^\circ$ , respectively. The only remaining suitable peaks are thus at  $17.7^\circ$  and  $54.8^\circ$  for  $\alpha$ -PbO and  $30.3^\circ$  and  $37.8^\circ$  for  $\beta$ -PbO.

Calibration curves for  $\alpha$ -PbO and  $\beta$ -PbO at each of these peaks were thus prepared by scanning the calibration standards in the appropriate  $2\theta$  intervals and determining the  $\alpha$ -PbO/NaF and  $\beta$ -PbO/NaF ratios respectively. At least six samples of each composition were prepared and analyzed in order to obtain several points for each of the peaks at each of the weight fractions. After discarding some erroneous data, the remainder were averaged to obtain a mean value of the intensity ratio at each composition. A least squares regression line was then fitted to these points, yielding the calibration curves which are presented in Fig. 3.

Samples of Barton Pot oxide material were obtained from three local battery manufacturers (A, B, and C) and analyzed by this method. The results, which are presented in Table 1, show that, not only is there considerable variation in the compositions of the lead oxide samples from the different manufacturers, but also samples taken on different occasions from the same manufacturer show variability.

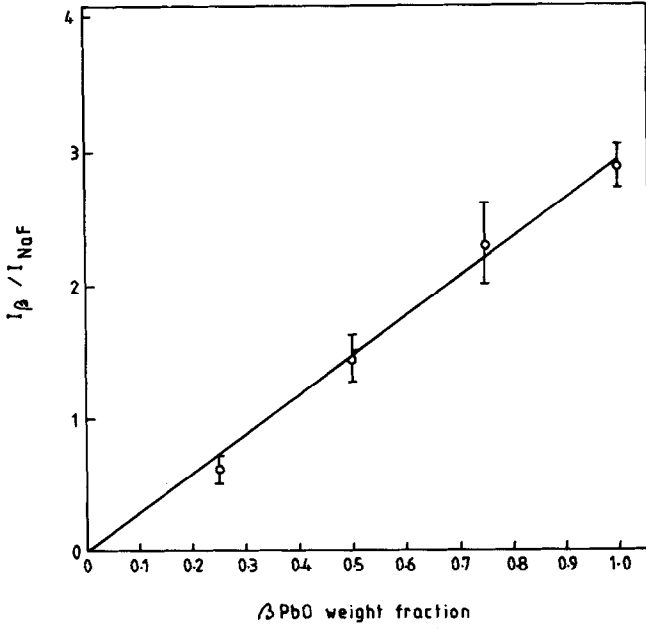


(a)

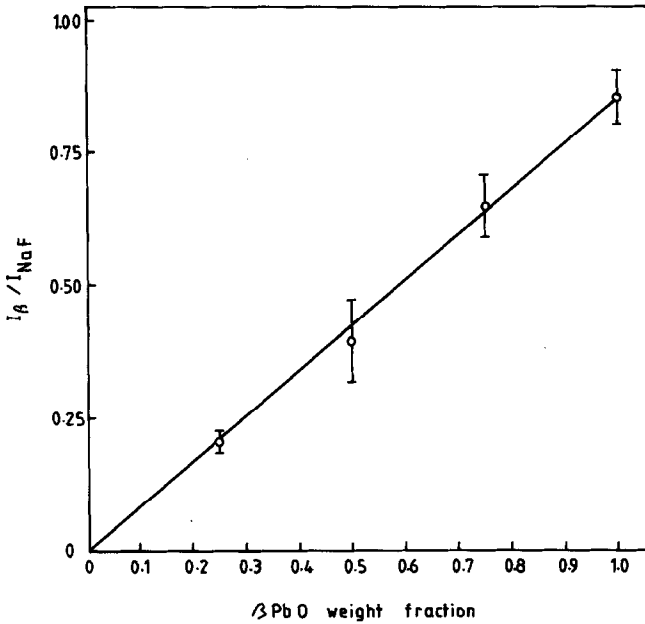


(b)

Fig. 3(a) - (b). (For legend please see overleaf.)



(c)



(d)

Fig. 3. Standard calibration curves for: (a)  $\alpha$ -PbO peak, scanning range,  $2\theta$ : 17.28 - 18.22°; (b)  $\alpha$ -PbO peak, scanning range,  $2\theta$ : 54.20 - 55.60°; (c)  $\beta$ -PbO peak, scanning range,  $2\theta$ : 29.90 - 30.95°; (d)  $\beta$ -PbO peak; scanning range,  $2\theta$ : 37.50 - 38.40°.



TABLE 1  
XRD determination of battery oxide composition

	Free Pb (%)	$\alpha$ -PbO (%)	$\beta$ -PbO (%)
Sample A <sub>1</sub>	25	70	5
A <sub>2</sub>	18	57	25
A <sub>3</sub>	28	59	13
Sample B	21	29	50
Sample C	29	67	4

## Conclusion

Although the exact effect of battery oxide composition on final battery performance has not, as yet, been resolved, it is generally accepted that the ratio of  $\alpha$ -PbO to  $\beta$ -PbO, together with the free lead, is important in determining the product distribution in the cured positive plates. The monitoring of the lead/lead oxide composition in the industrial process should therefore be of considerable importance in ensuring adequate quality control in the manufacturing process. In the present study, a method has been developed for the quantitative determination of the lead/lead oxide composition using X-ray diffraction. The method is currently being used to monitor changes in the composition of the lead/lead oxide produced by a local battery manufacturer, with variations in the operating conditions of the Barton Pot.

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