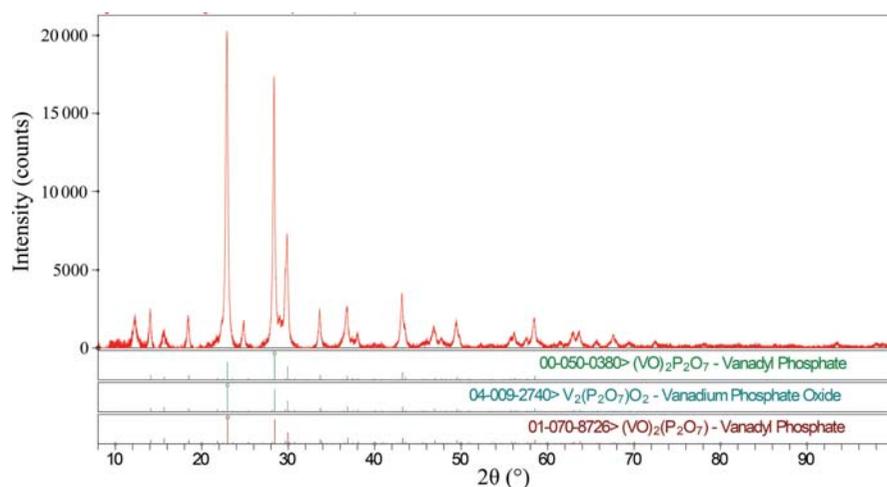
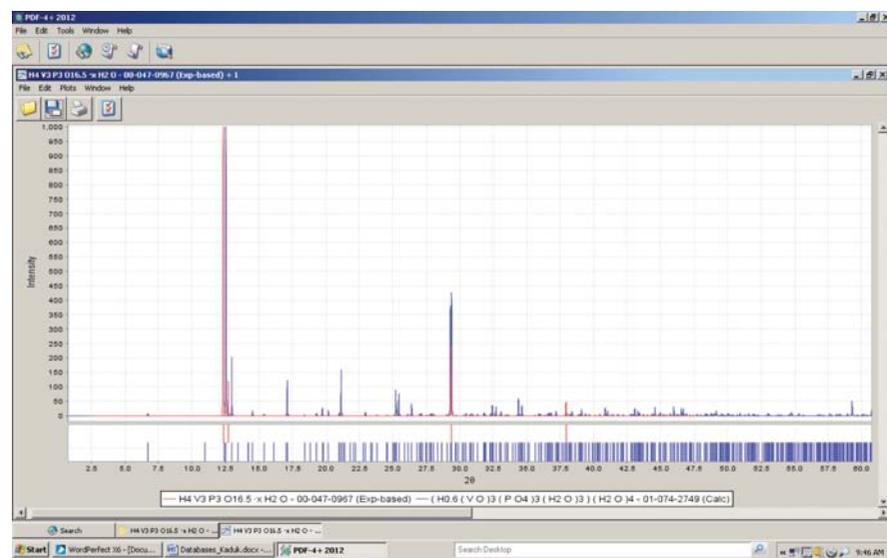


## 3.7. CRYSTALLOGRAPHIC DATABASES



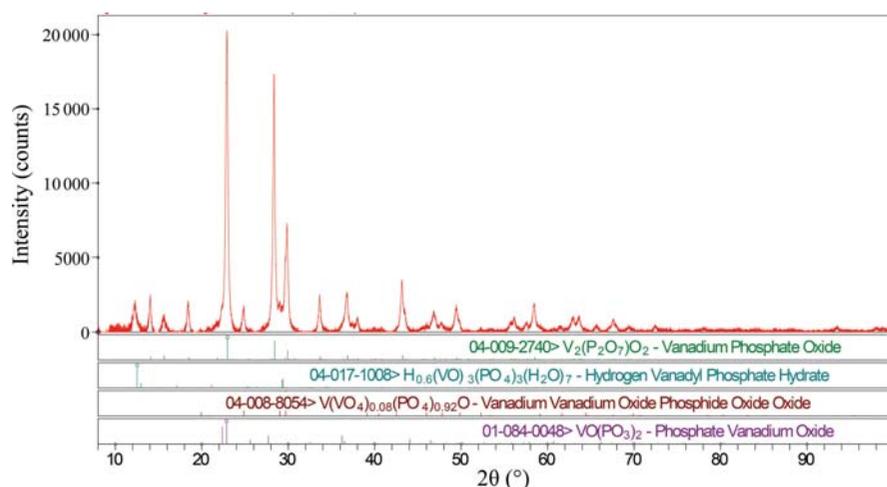
**Figure 3.7.4**

The results of applying a commercial search/match program (*Jade 9.5*; Materials Data, 2012) to the (background-subtracted,  $K\alpha_2$ -stripped) powder pattern of a butane-oxidation catalyst. The first three patterns in the hit list had equivalent figures of merit. The PDF entries 00-050-0380 and 04-009-2740 had Star quality marks and 04-009-2740 contained the atomic coordinates necessary for a Rietveld refinement. Additional peaks are apparent. The phases that give rise to them were identified using the native capabilities of the Powder Diffraction File.



**Figure 3.7.5**

Comparison of the low-quality experimental PDF entry 00-047-0967 with the high-quality calculated pattern 01-074-2749 located by searching the experimental pattern against the rest of the PDF. The similarity in patterns and chemistry demonstrated that the two phases were the same and that the coordinates used to calculate entry 01-074-2749 could be used in a Rietveld refinement of a butane-oxidation catalyst.



**Figure 3.7.6**

The four crystalline phases identified in a butane-oxidation catalyst.

3.7.2.4.4. *Isocracker sludge*

An isocracker is a refinery unit which simultaneously carries out cracking and isomerization reactions to produce more high-octane gasoline. A black deposit isolated from such a unit was surprisingly crystalline (Fig. 3.7.9; files NALK157.gsas, NALK157.raw and padv.prm). It was easy to identify small concentrations of elemental sulfur, pyrrhotite-4M (now called pyrrhotite-4C), haematite, lepidocrocite and dolomite, but the major peaks did not match well those of any entry in the PDF.

It seemed likely that a mineral-related phase would serve as a structural prototype for an apparently new phase, so two separate searches for mineral-related phases with one of their three strongest peaks in the  $d$ -spacing ranges  $7.09 \pm 0.03$  and  $5.57 \pm 0.03$  Å were combined. The two hits in the search list were both uranium minerals. These seemed unlikely in a refinery deposit(!). Widening the search ranges to  $7.09 \pm 0.10$  and  $5.57 \pm 0.07$  Å yielded rasvumite,  $KFe_2S_3$  (PDF entry 00-033-1018), as the second entry in the hit list.

The fit to the major peaks in the deposit was reasonable, but there should not be any potassium in a refinery deposit and none was detected in a bulk chemical analysis. When the jar containing the deposit was opened, it smelled strongly of ammonia. Ammonium and potassium ions are about the same size and often form isostructural compounds. The infrared spectrum of the deposit was dominated by bands of ammonium ions.

The potassium in the structure of rasvumite (PDF entry 01-083-1322, used as a reference) was replaced by nitrogen. Analysis of potential hydrogen-bonding interactions yielded approximate hydrogen positions in the ammonium ion. These positions were refined using a density-functional geometry optimization. This model yielded a satisfactory Rietveld refinement (Fig. 3.7.10) and the quantitative analysis 45.7 (2) wt%  $(NH_4)Fe_2S_3$ , 12.8 (4) wt%  $S_8$ , 22.0 (6) wt% lepidocrocite ( $\gamma$ - $FeOOH$ ), 5.5 (5) wt% haematite ( $\alpha$ - $Fe_2O_3$ ), 6.6 (3) wt% pyrrhotite-4C ( $Fe_7S_8$ ) and 6.6 (3) wt% dolomite [ $CaMg(CO_3)_2$ ; limestone environmental dust]. The powder pattern and crystal structure of  $(NH_4)Fe_2S_3$  are now included in the PDF as entry 00-055-0533.

3.7.2.4.5. *Amoxicillin*

The amoxicillin powder from a commercial antibiotic capsule was highly crystalline. Its powder pattern (files kadu918.gsas, KADU918.raw, d8v3.prm and KADU921.rd) was matched well by the PDF entries 00-039-1832 and 00-033-1528 for amoxicillin trihydrate, but there was an additional peak at a  $d$ -spacing of 16.47 Å ( $5.37^\circ 2\theta$ ). With such a low-angle peak, it seemed prudent to measure the pattern again