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## **DIFFERENT DISSOLUTION PROCEDURES FOR ANALYSIS OF TITANIUM(IV) OXIDE WHITE PIGMENT**

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### **ABSTRACT**

Various ways of sample preparation for subsequent analysis of titanium(IV) oxide white pigment are represented. Three different procedures: digestion in various mediums, lithium metaborate fusion and pressure dissolution with hydrofluoric acid are precisely represented and considering accuracy, precision, blank values, time of analysis and general procedure's simplicity, the last procedure is undoubtedly the most appropriate one.

### **INTRODUCTION**

In spite of the fact that titanium(IV) oxide white pigment is indispensable in our everyday life, very few procedures for its analysis are described in literature [1-14]. Among the most common approaches of sample dissolution described in these articles are either treating the pigment with different mixtures of various chemicals and subsequent extraction or slurry introduction accompanied by electrothermal or flame atomic absorption spectrometry. The main imperfections of the before mentioned dissolution procedures are long duration time of the sample preparation for the first procedure and poor precision for the second one. Nowadays, some information about pressure dissolution in conventional and microwave ovens using various acids and about solid sampling following by electrothermal atomisation are also available.

While neither of the already described dissolution procedures are suitable for our purposes, we decided to try finding another simple and rapid dissolution procedure which would give accurate and precise results for concentration of trace metals in titanium(IV) oxide white pigment. After detailed study of the literature data about the already known dissolution procedures which enables the determination of trace elements in oxides of refractory elements, three different ways of sample preparation were experimentally performed [15-48]. First, digestion of samples with various acids followed by spectrophotometric determination of iron were investigated. Due to some considerable imperfections which this procedure has, it was replaced first by lithium metaborate fusion and finally, the pressure dissolution with hydrofluoric acid took place.

## **EXPERIMENTAL**

### *Apparatus*

For spectrophotometric determination of iron concentration with o-phenantroline Iskra spectrophotometer model HPV210 was used. Absorbances were measured at 510 nm.

A Perkin-Elmer model 4000 flame atomic absorption spectrophotometer with conventional and high performance nebuliser (HPN) and Perkin-Elmer model 2280 with HGA 400 AAS were used. For atomic absorption measurements, standard instrumental parameters were applied using background correction.

Results obtained by X-ray fluorescence spectrometric method were achieved on a Philips PW 1404 instrument interfaced to a Philips P 2723-302 computer for automatic control and data processing at standard conditions; a Cr anode X-ray tube was used throughout. For pressure dissolution of samples four 25 ml and four 30 ml teflon vessels made by two different producers were used.

### *Reagents*

All reagents used were of analytical reagent grade.

### *Digestion*

1.0000g of pigment was treated with 50 ml of various acids or their mixtures. After heating for some hours, suspensions were filtered and absorbances were measured. Regarding the results of these preliminary experiments, five different samples of titanium(IV) oxide were digested in 6 M hydrochloric acid for three hours. Each sample was analysed in at least three replicates. For the determination of the element's concentration standard addition technique was used.

### *Lithium Metaborat Fusion Procedure*

The detailed description of this sample dissolution procedure is explained in already published article [13].

### *Hydrofluoric Acid Decomposition Method*

Before the decomposition procedure was developed, several reagents, their mixtures and different experimental conditions (time, temperature), at which quantitatively dissolution takes place, were examined.

1.0000 g of sample was transferred to PTFE vessels. 5 ml of HF was added and pressure dissolution was took place at 150°C for two hours. After cooling the PTFE vessels, the solutions were quantitatively transferred to 25 ml polypropylene volumetric flasks. Three different volumes of standard solutions were added and absorbances were measured. Blank solution was prepared for each experiment separately.

In the above described way achieved results were statistically treated and compared to results obtained by X-ray fluorescence spectrometry, which is used as every day analytical method for the determination of traces of elements in titanium dioxide white pigment samples [49-51].

## **RESULTS AND DISCUSSION**

### *Digestion*

As already mentioned , digestion of the same sample with different reagents, represented in Table 1, was studied first.

**Table 1. Reagents and their mixtures used for digestion of titanium(IV) oxide white pigment samples**

Acid	Mixtures						
	A	B	C	D	E	F	G
HCl	1M	6M	1M	1M	1M	3M	
HNO <sub>3</sub>			5M	1M	3M	1M	
HClO <sub>4</sub>							1M

On the basis of measured absorbances and other procedures' characteristics, 6M HCl was chosen for all succeeding experiments. Obtained results and results achieved by XRF technique, are shown in Table 2.

**Table 2. Results obtained by the digestion procedure followed by AAS technique and by XRF method**

Sample	c(Fe) <sub>AAS</sub> mg/kg	S <sub>rel.</sub> %	c(Fe) <sub>XRF</sub> mg/kg
A	45	6	38
B	55	25	28
I	32	14	19
J	26	4	32
K	12	-	10
L	12	-	16
M	25	22	42
U	30	7	37
Z	32	10	29

Statistical comparison of the results obtained by the digestion procedure followed by AAS technique and by XRF method showed, that these two methods do not give statistically different results at 95 % confidence level. Such at a first sight surprisingly statistical conclusion is a consequence of a high imprecision of the results obtained by AAS technique which is due to very low measured absorbances. In order to avoid this problem, the procedure for quantitatively sample dissolution with lithium metaborate followed by hydrochloric melt dissolution was developed.

*Lithium metaborate fusion*

Since detailed description of given procedure has already been published [13] only the main ascertainments will be discussed here. First, different experimental conditions i.e. the ratio of masses of  $\text{LiBO}_2$  and  $\text{K}_2\text{CO}_3$  and concentration and volume of HCl were examined. As optimal procedure for quantitative dissolution of pigment and subsequent determination of concentration of the elements in the solution, a procedure where a melt, obtained by fusing 0.2000 g of sample with 1.0 g of  $\text{LiBO}_2$  and 4.0 g of  $\text{K}_2\text{CO}_3$  in platinum crucible at  $1000^\circ\text{C}$  was quenched in 150 ml of hot HCl acid. Concentration of HCl depends on the further treating of the solution. If the iron concentration was determined spectrophotometrically and extraction was used as a separation step, 6 M HCl was used, while in all other cases, where the concentrations of elements (Al, Cu, Cr, Fe, Sb, V) was determined either by flame or electrothermal atomic spectroscopy, 3M HCl was used [52]. The main imperfection of the above described sample dissolution procedure is high absorbances of blank solutions, which disable the determination of elements which are present in lower concentration i.e. few ppm. In Table 3 results for spectrophotometric determination of iron are shown.

**Table 3. Experimental results for spectrophotometric determination of iron in titanium(IV) oxide white pigment by o-phenantroline**

Determinations	Absorbances	
	Blank	Sample
1	0.006	0.028
2	0.008	0.026
3	0.019	0.025
4	0.026	0.026
5	0.058	0.059
6	0.025	0.028
7	0.014	0.019
8	0.035	0.055
9	0.021	0.028
10	0.021	0.021

The detailed further investigations showed that the high blank values are caused by leaching of elements from platinum crucibles [53, 54]. The experiments showed that the most important component in this process is the amount of  $K_2CO_3$  and that after each fusion the platinum crucible is lighter for about 20 mg. Considering described important deficiency of this sample dissolution procedure which is suitable only for quantitative determination of elements in higher concentration range, another procedure for titanium(IV) oxide white pigment dissolution was developed. In Table 4 results obtained by the above described procedure for the concentration determination of antimony are shown and compared with results achieved by XRF method.

**Table 4. Results for antimony in titanium(IV) oxide white pigment samples obtained by flame AAS and XRF method**

Sample	Concentration (%)	
	AAS	XRF
VA	0.02	0.02
VB	0.04	0.02
VC	0.13	0.12
VD	0.04	0.03

#### *Pressure pigment dissolution*

It is already well known that among various acid and their mixtures only hydrofluoric acid quantitatively dissolute the titanium(IV) oxide white pigment, but its aggressive nature against glass should be appropriately overcome. For that purpose, boric acid was frequently mentioned, but according to our experience, it is very unsuitable for quantitative trace elements determination. Nowadays, the problem could be easily overcome if all accompanied equipment is made from appropriate material, in that case from polypropylene (PP). The procedure where 1.0000g of titanium(IV) oxide white pigment sample and 5 ml of hydrofluoric acid is heated to 250°C for two hours was used for different types of titanium(IV) oxide white pigment's samples. The subsequent determination of elements' concentration could be easily performed, obtaining precise results. Considering this and the fact that no insurmountable troubles during performing

these analyses were observed, this dissolution procedure is proposed as the most suitable one for the subsequent trace element determination in titanium(IV) oxide white pigment.

## CONCLUSION

From represented results is evident that the pressure dissolution of titanium(IV) oxide white pigment with hydrofluoric acid is undoubtedly the most suitable way of quantitative dissolution of this kind of samples. While the imperfections of the digestion method and the lithium metaborate fusion procedure could be eliminated, the only accompanied trouble with this procedure i.e. the aggressive nature of hydrofluoric acid, could easily be overcome by using the equipment from appropriate material. The precision of the pressure dissolution procedure followed by AAS method for elements' concentration determination is also acceptable and the time required for complete quantitative determination of seven elements do not exceed four hours and is therefore highly recommended as regularly used analytical procedure for trace element determination in titanium(IV) oxide white pigment samples. Moreover, it can also serve as an alternative method to routine XRF method and particularly for analysing standards for the later method.

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## POVZETEK

V članku so opisani različni postopki raztapljanja belega pigmenta titanovega(IV) oksida. Izmed izluževanja v različnih medijih, raztapljanja taline z litijevim metaboratom v klorovodikovi kislini in raztapljanja vzorca pod tlakom s fluorovodikovo kislino, se je slednji postopek izkazal kot najprimernejši, upoštevajoč pravilnost in natančnost postopka, slepe vrednosti in čas analize.