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ATOMIC ABSORPTION AND RADIATION SCATTER DETECTION IN THERMAL ANALYSIS. REACTIONS OF ZINC OXIDE WITH ORGANOHALIDES

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ABSTRACT

Flame atomic absorption spectrometer is coupled to a modified thermoanalytical quartz furnace for the element specific detection of the evolved species. The potentiality of this method is demonstrated here by studying the reactions of ZnO with several halogen donors used in flame inhibition technology. Replacing the analytical flame for a flow cuvette, the radiation scatter of organic particulates is detected and compared to DTG curves.

INTRODUCTION

The novel trends in optical atomic spectrometry /OAS/ include the separation of vaporization and atomization-excitation processes to attain improvements in this discipline. Some of the concepts and techniques of this kind can also be utilized in thermal analysis, as it appears from a recent review on this particular topic[1]. The element specific detection of the volatile decomposition products using e.g. an AA spectrometer offers essential complementary information to those available by the known TA techniques.

MEASURING METHODS

Detailes of instrumentation and general conditions have been described elsewhere[2]. A windowless version of the flow cuvette was used in the present studies for radiation scatter detection[3]. Absorbance vs temperature curves /AT-curves/ were directly recorded in monitoring both the atomic absorption signal and the attenuation caused by radiation scatter /apparent absorption signal/. The DTG curves of polyvinyl chloride /PVC/, Cerechlor and Flammex /bromine donor/ were separately recorded[4] by means of a Derivatograph /Hungarian Optical Works/.

RESULTS AND DISCUSSION

The DTG curves of organic halogen donors /curves b in Fig. 1/

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are informative about the release of both inorganic and organic species taking part in heterogeneous reactions with ZnO_s /see below/. Aggregates formed from certain fractions of organic species are separately detected by radiation scatter measurement /curves a in Fig. 1/. Therefore, the formation of the inorganic reactants and that of the organic reactants might be differentiated by comparing the DTG and AT curves in Fig.1. Gas titrimetric /DTDT/ measurements with PVC has revealed[4] that the low temperature peak /curve 1b/ corresponds to HCl evolution and from the curve 1a it is seen that organic species are evolved dominantly at higher temperature. Determination of the inorganic species evolved from Cerechlor /curves 2a, 2b/ and from Flammex /curves 3a, 3b/ has not been completed. However, it is expected form curves 2 and 3 that evolution of organic species precedes that of the inorganic species in a small extent, but more dominantly the two processes are overlaping.

From these findings and from the curves in Fig. 2, it can be concluded /as a brief/ that both halogenation and reduction of ZnO_s are taking place in the presence of organohalides resulting in the evolution of zinc halide and zinc vapour species respectively.

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Fig. 1. Radiation scatter AT-curves /a/ and inverted DTG curves /b/ of organohalides. Pt sample holder, N_2 atmosphere, 50 °C/min heating rate. Sample mass of 5 and 100 mg for AT-curves and DTG curves respectively. 1 - PVC; 2 - Cerechlor; 3 - Flammex.

Fig. 2. AT-curves of ZnO mixed with different organohalides in N_2/curves a/ and in air /curves b/ atmospheres. Pt sample holder, 50 °C/min heating rate, 1.5 mg sample mass, Zn: halogen=1:2/mixing ratio/. 1 - ZnO+PVC; 2 - ZnO+Cerechlor; 3 - ZnO+Flammex.

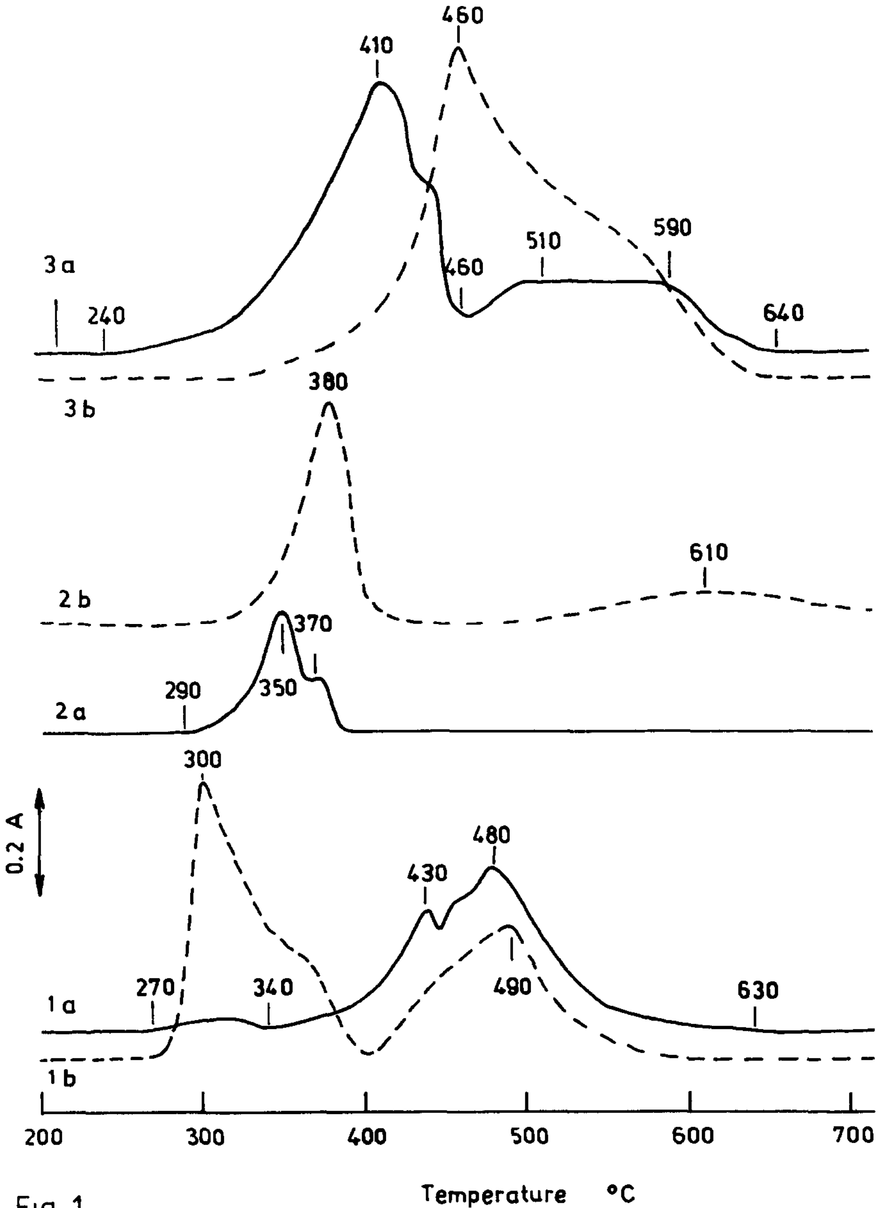
460
410
3 a
240
460
510
590
640
3 b
380
610
2 b
370
2 a
290
350
300
0.2 A
480
430
270
340
490
630
1 a
1 b
200
300
400
500
600
700
Temperature °C

Fig 1

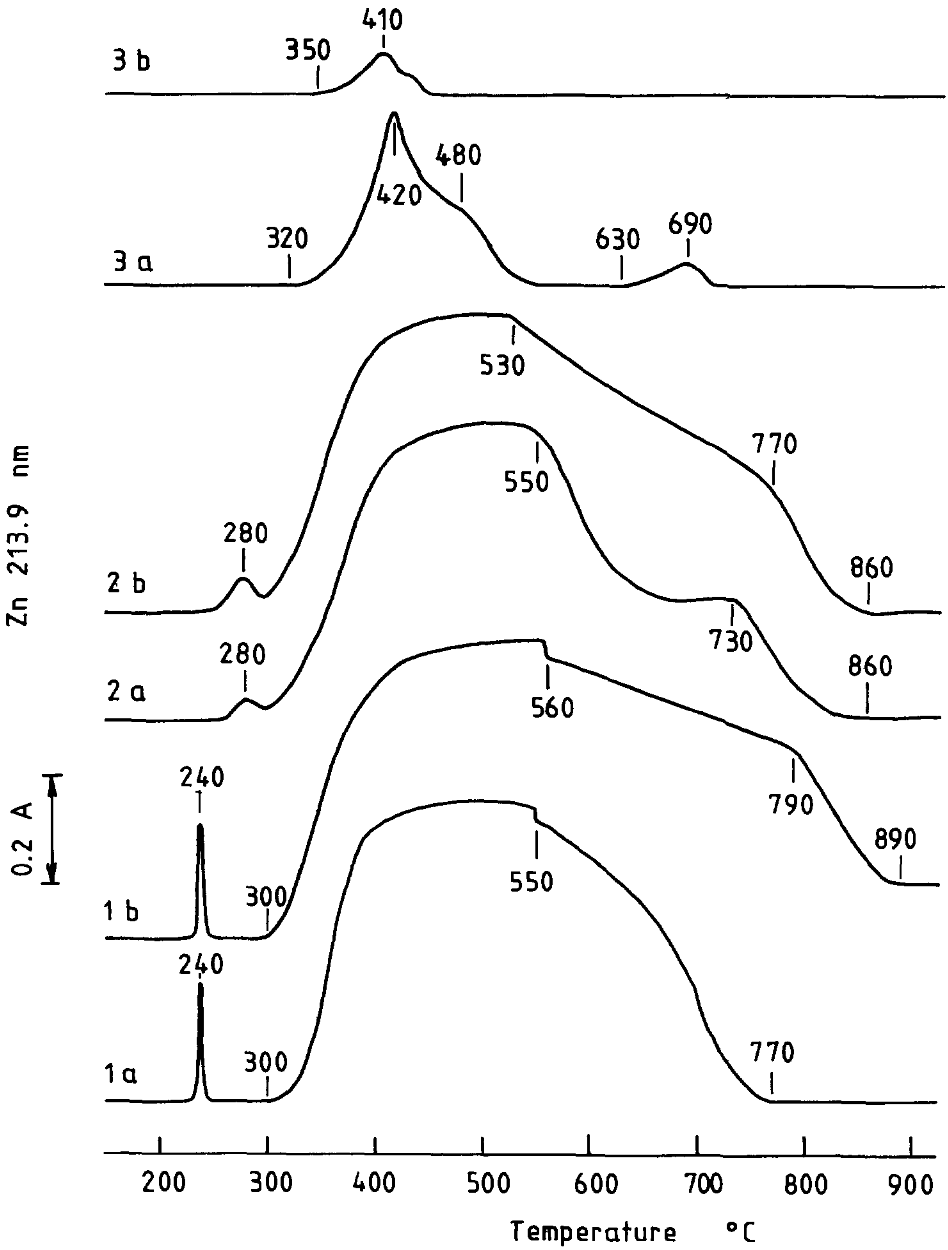
3 b
350
410
3 a
320
420
480
630
690
530
770
550
2 b
280
860
730
2 a
280
860
560
790
890
1 b
240
300
550
1 a
240
300
770
Zn 213.9 nm
0.2 A
200
300
400
500
600
700
800
900
Temperature °C

Fig 2