

Applications of *PulseTA*[®] to the investigation of fluorides An attempt to calibrate HF

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Abstract

Several procedures for the calibration of MS signals such as $m/z = 19$ (F^+) representing hydrogen fluoride, HF, have been tested in order to achieve a reliable quantitative description of the thermal behaviour of fluorides and/or fluoride hydrates by applying the recent *PulseTA*[®] technique (PTA). Instead of desirable indirect calibration methods without the use of the corrosive HF, only the direct injection of 40% aqueous HF gave satisfying results. A differential calibration procedure, recently reported in literature, has been successfully applied. It will be demonstrated that both the calibration of $m/z = 18$ for water and $m/z = 19$ for hydrogen fluoride can be performed in a correct way for each mass number. But their joint application to the quantitative description of a given compound revealed to be difficult if not impossible. This is interpreted in terms of the extreme properties of fluorides simultaneously liberating H_2O and HF.

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1. Introduction

The solid state chemistry of halides or halometalate complexes is directly related to the exact knowledge of the role and the extent of pyrohydrolysis which occurs if halides were subjected to heating processes. Pyrohydrolysis means the replacement of the metal-bound halogen atom by hydroxyl groups and/or oxide ions which may proceed in the reaction of solid halides at higher temperatures with water vapour. Water vapour is, to a more or less significant extent, practically omnipresent in all (inert) gases utilized in usual laboratory experimental setups regardless of the pretreatment by vacuum procedures, drying columns or whatsoever. Besides the oxide phase, pyrohydrolysis produces the corresponding hydrogen halide, e.g. HCl in the case of chlorides. Pyrohydrolysis of fluorides yields hydrogen fluoride, HF, which is known for its especially high reactivity towards glassy, metallic or ceramic surfaces.

It is, therefore, of crucial importance for the evaluation of the impact of heating processes on the phase composition of fluorides to know the extent of surfacial or bulk substitution of fluoride by oxygen or hydroxyl groups, i.e. to know the fraction of fluoride that has been transformed into an oxide

or a hydroxofluoride. As the exchange F/OH does not affect a detectable mass change, thermogravimetric (TG) analysis is not an appropriate tool for investigation. On the other hand, if the thermoanalytical (TA) equipment is coupled to an evolved gas analysis (EGA) device, e.g. to MS, changes in the product gas composition are easy to follow. Especially promising is the extension of coupled TA devices by the recent *PulseTA*[®] technique (PTA) which has been developed in order to significantly enlarge the interpretation possibilities of TA curves [1–3]. After preceding calibration of the TA–MS apparatus, which may be performed in different ways [4], the PTA technique allows for a quantitative evaluation of ion current (IC) curves and can relate a given IC signal to a mass loss. This can permit the differentiation between overlapping partial reactions in a given TG step as well as the simultaneous monitoring of the chemical effects of dosed gases on the sample at elevated temperatures.

Two mass numbers can be followed to represent HF: $m/z = 19$ (F^+) or 20 (HF^+) both with low intensity contributions by other ions (H_3O^+ and $H_2^{18}O^+$, respectively). Mostly, the intensity for $m/z = 19$ is higher than for $m/z = 20$ which led to the conclusion to preferably regard the mass number 19.

Up to now, a quantitative description of the HF evolution during thermal processes is lacking due to the fact that no calibration seemed to be possible. This is due to the known fact that no solid fluoride exists which would fulfil two essential requirements: easy handling in an ambient atmosphere without

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(fast) hydrolysis and, yet more important, liberating an exactly known amount of HF in a stoichiometrically defined reaction. The first attempt to make use of a stoichiometrically ill-defined phase such as solid $\text{NaHF}_2 \cdot n\text{H}_2\text{O}$, has been described recently [5]. But the direct introduction of HF into a TA equipment had always been avoided in order to prevent corrosion. Furthermore, the usual “chemical” calibration as proposed in [5] is correctly valid only for the liberation temperature of HF in the calibration run, i.e. 200–250 °C in the case of NaHF_2 . As the intensity of the MS signals in a *Skimmer*[®] system is temperature-dependent¹, the validity of the calibration factor has to be verified if it shall be applied for the quantification of MS signals recorded at higher temperatures, e.g. 600–800 °C. But this was impossible by two reasons: firstly, no substance exists which liberates HF at these temperatures; secondly, one is rather unwilling to take the risk of injecting gaseous HF in a TA apparatus in this temperature range.

It was our aim, therefore, to develop a calibration method without direct use of HF. The idea was to measure the temperature-dependent decrease of the integral IC intensity for harmless permanent gases and even liquids. The mean value of their intensity decrease was supposed to be approximately the same as for HF thus allowing for an estimation of the temperature-dependent variation of the calibration factor, which must have been precedingly determined in a separate procedure.

In the present paper we will show that this calibration method could not fulfil the expectations but had to be replaced by a direct liquid injection procedure. Furthermore, we will show that, due to the extraordinary complex behaviour of fluorides, even this valid calibration method does not yield in each case reliable interpretations. Some examples shall illustrate it.

2. Experimental

2.1. Chemicals

FeF_3 (Merck) and CrCl_3 (Aldrich) were used as commercially available, whereas $\alpha\text{-AlF}_3$ was obtained by dehydration of $\beta\text{-AlF}_3 \cdot 3\text{H}_2\text{O}$ under the special synthesis conditions of the “self-generated atmosphere” existing in Q-crucibles [7,8]. MgF_2 powder was obtained by mortaring an optical window of monocrystalline MgF_2 purchased by Korth Kristalle GmbH (Kiel, Germany). $\text{Na}_3\text{AlF}_6 \cdot 0.6\text{H}_2\text{O}$ was obtained in crystalline form via an alkoxide sol–gel process as described in [9], whereas the hydroxy fluorides such as $\text{AlF}_{2.6}(\text{OH})_{0.4} \cdot 0.12\text{H}_2\text{O}$ have been synthesized and characterized as given in [10].

The permanent gases oxygen 4.8, hydrogen 4.8, carbon dioxide, argon 5.0 were taken from pressure bottles purchased by Messer-Griesheim.

¹ The temperature dependence of the IC signals is due to the constructive design of the *Skimmer*[®] system. As the orifice system for the gas sampling for the MS has nearly the same temperature as the sample, which makes the great advantage of a *Skimmer*[®] coupling system, one of the unavoidable disadvantages is that the MS signals become temperature-dependent. This does not represent a real problem—one should only know this temperature dependence [6].

2.2. Apparatus

The PTA investigations have been performed by utilizing a simultaneously coupled TA–MS device. A NETZSCH thermoanalyzer STA 409 C *Skimmer*[®], equipped with a BALZERS QMG 421 and a *PulseTA*[®] unit, was used to record the thermoanalytical curves (T, DTA, TG, DTG) together with the IC curves in the multiple ion detection (MID) mode [11,12]. A DTA–TG sample carrier system with platinum crucibles (baker, 0.8 ml) and Pt/PtRh10 thermocouples was used. Samples of 20–40 mg each were measured versus empty reference crucible. A constant purge gas flow of 70 ml/min nitrogen (N_2 5.0, Messer-Griesheim) and a constant heating rate of 10 K/min were applied. The raw data have been evaluated utilizing the manufacturer’s software PROTEUS[®] (v. 4.3) and QUADSTAR[®] 422 (v. 6.02) without further data treatment, e.g. such as smoothing.

The injection of gases has been performed via the injection loops (500 μl) of the PTA unit coupled to usual pressure bottles whereas for the injection of liquids a microliter syringe (2 μl) and a heated steel loop with GC injector (110 °C) and silicon septum was used.

All heating runs of fluorides were preceded by a cleaning run up to 1200 °C of the empty measuring cell in order to ensure desorption of HF from the apparatus parts originating from the fluoride measured before. From time to time, a second cleaning run of the empty apparatus proved the completeness of the HF desorption.

3. Results

3.1. The temperature-dependent calibration factor

Fig. 1 shows the IC curves for a sequence of 8 or 9 pulses of three permanent gases and liquid water. The injections have been performed for each substance in a separate heating run up to 950 °C into the TA cell without a sample. Due to the different flow conditions in the liquid injection system, a greater tailing is observed for water.

Fig. 2 shows the integral intensity of the pulses injected in the sequence presented in Fig. 1. The intensity has been related to that of the first pulse which was set as 100%. Oxygen, argon, 1-butene, carbon dioxide, and water behave as expected whereby the greater deviation in the case of water reflects the greater volume error which occurs when injecting liquids with a microliter syringe. 1-Butene can be followed up to 450 °C only because of the beginning pyrolysis. Hydrogen revealed to be inappropriate as the peak area increases with rising temperature. This is a result of the strongly differing thermophysical properties of hydrogen compared with the other gases (heat capacity, viscosity, flow properties). Furthermore, above 250 °C, hydrogen vigorously reacts with residual amounts of oxygen in the purge gas which can be also registered in the DTA traces (not shown here).

It is noteworthy to mention that the decrease of the integral intensity of the pulses at higher temperatures, which is characteristic for the utilized *Skimmer* apparatus, revealed to be lower than expected for this temperature range (25–950 °C) – it amounts to values between 5% for H_2O and 23% for CO_2

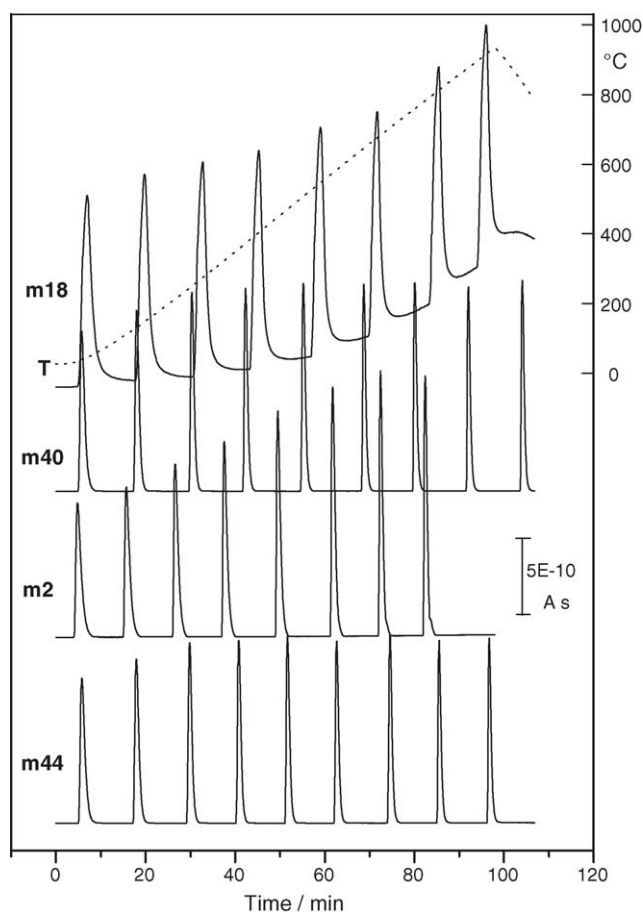


Fig. 1. IC curves for the mass numbers 18(H_2O^+), 40(Ar^+), 2(H_2^+), and 44(CO_2^+) for the injection of 2 μl $\text{H}_2\text{O}(\text{l})$ or of 500 μl of the permanent gases upon heating with 10 K/min in nitrogen.

whereby the differences are related to the different thermophysical properties of the gases.

The bold line represents the presumed curvature for the evolution of the peak area for HF. For a given temperature of, e.g. 700 °C, which would represent a relevant temperature range for the investigation of pyrohydrolysis (see above), only 8–10% peak area decrease has to be taken into account. One obtains an increased calibration factor $F_{\text{Cal}}(m19)$ of 6.7 E7 compared to 6 E7 mg/As. This correction, of course, would not significantly change the calculated mass loss values.

Nevertheless, we applied the corrected calibration factor to the evaluation of a series of fluorides and hydroxofluorides as the mass changes followed by TG were rather weak (between 0.1 and 1 mg for the pyrohydrolysis) and a maximum precision was desirable. It was established, however, that no reasonable relation could be drawn between a thermogravimetrically registered mass loss and a mass loss determined by quantification of the signal $m/z = 19$. Generally, the mass losses determined by PTA are considerably too high for HF and do not allow for an appropriate interpretation.

3.2. The differential calibration method using liquids

As the “chemical” calibration of the MS apparatus via the decomposition of a solid fluoride together with the described

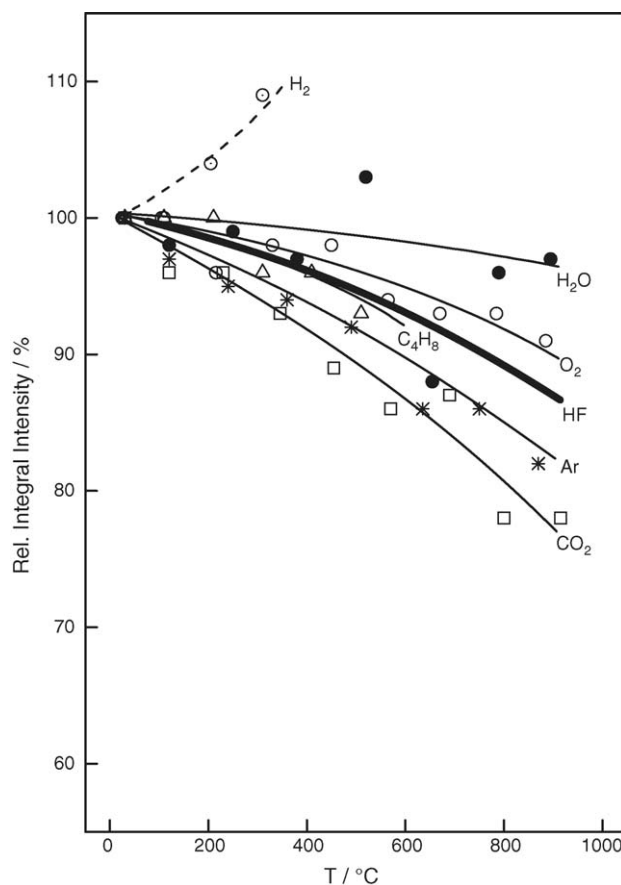


Fig. 2. Temperature dependence of the integral intensity of the IC signals for the pulse sequence of the different gases injected (cf. Fig. 1) together with the estimated intensity evolution for HF (bold line).

correction does not yield reasonable values, we finally attempted to directly inject aqueous HF. A recent study reported on a differential method for the calibration with liquids such as ethanol and seemed to be appropriate for HF as well [13]. The essential steps of the procedure, which reflect particularities of the apparatus design, are as follows:

- (1) Registration of the IC zero line with empty apparatus for the mass number to be followed;
- (2) Balance arresting and opening of the measuring cell without stopping the measurement;
- (3) Addition of a certain amount of the liquid, e.g. 5 μl , to the crucible utilizing a syringe;
- (4) Closing apparatus, balance release and continuing the measurement;
- (5) Registration of the isothermal evaporation of the substance, e.g. at room temperature;
- (6) Relating a selected TG interval (Δm) to an area under the IC curve.

Fig. 3 illustrates the successful testing of the procedure with water. A calibration factor $F_{\text{Cal}}(m18)$ of 0.71 E7 mg/As is obtained which corresponds well to the value of 0.76 E7 that has been determined separately via the dehydration of $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$. This means that the proposed procedure is quite

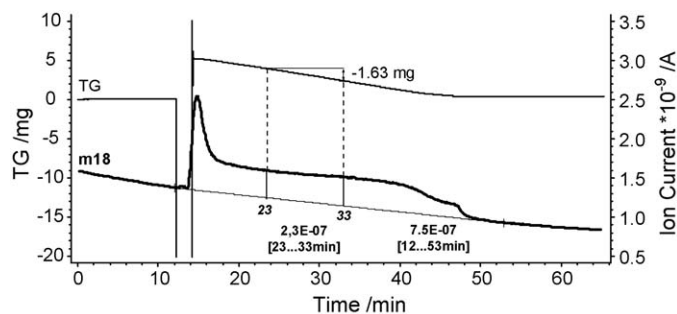


Fig. 3. Differential calibration of the TA cell at 25 °C by injection of 5 µl liquid water. The TG jump represents the balance arrest required for the oven lifting and the addition of the liquid into the Pt crucible. A TG interval with constant evaporation rate, e.g. between 23 and 33 min, has been chosen for the area integration.

appropriate for calibration. The methodology was now applied to the case of aqueous 40% HF. Here, the situation is more complicated as the liquid forms an azeotrope, a problem on which already focused Cozzani and co-workers [14] regarding the coupling of MS or FTIR to a thermobalance. For a correct determination of the calibration factor one has to ensure steady state conditions for the evaporation in order to know the percentage of the component in the gas phase, i.e. to know which fraction of an observed mass loss corresponds to the component one is interested in. In the case of the system HF–H₂O, the azeotropic concentration is 38% HF [15].

Fig. 4 illustrates that the required steady state conditions are rather difficult to realize in the case of aqueous HF. A quantity of 5 µl 40% HF is not sufficient to reach the evaporation equilibrium as the HF molecule is extremely strongly adsorbed on apparatus parts from the gas phase. Therefore, with a considerable delay of approximately 15 min, one detects HF in the purge gas only. If the added amount of aqueous HF is greater, steady state conditions are finally reached which is expressed in a more or less horizontal part of the IC curve for $m/z=19$ – this means that a constant ratio of HF and H₂O evaporates, and this should represent the azeotropic concentration with 38% HF. This is demonstrated in Fig. 5. Based on this procedure, a calibration factor of $F_{\text{Cal}}(m19)$ of 0.61 E7 mg/As is obtained, i.e. one tenth of the factor determined as described in the preceding section.

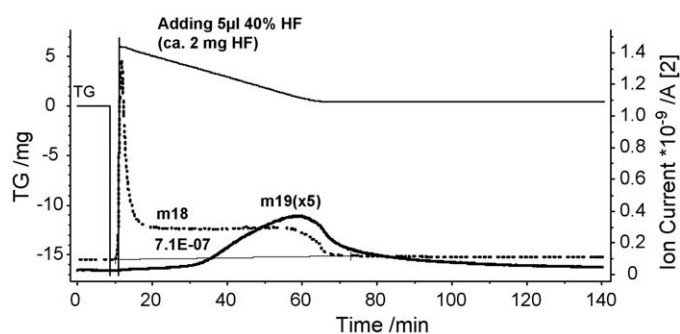


Fig. 4. Attempt for the differential calibration of the TA cell at 25 °C by injection of 5 µl 40% HF. The HF detection is remarkably delayed, whereas the water behaves as shown in Fig. 3.

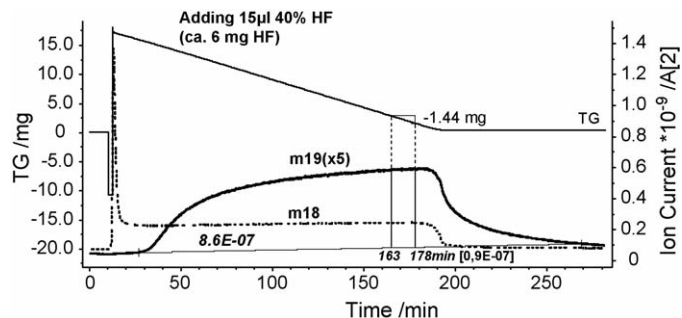


Fig. 5. Differential calibration of the TA cell at 25 °C by injection of 15 µl 40% HF. The HF detection is delayed as shown in Fig. 4, but due to the greater amount of HF and, consequently, another time scale, steady state conditions can be reached at the end of the measurement run.

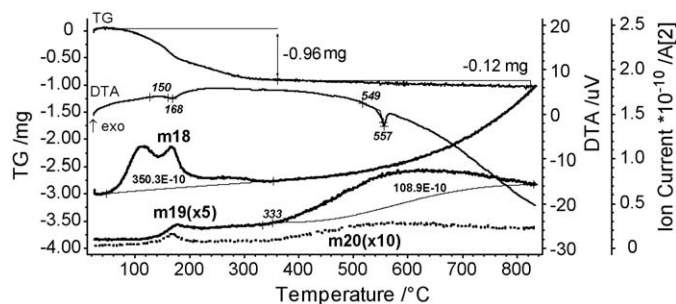


Fig. 6. TA–MS curves of Na₃AlF₆·0.6H₂O exhibiting the reversible LT–HT phase transition of Na₃AlF₆ [16] together with the IC curves for the mass numbers 18(H₂O⁺), 19(F⁺), and 20(HF⁺). Note that the contribution of HF⁺ to $m/z=20$ predominates that of ¹⁸H₂O⁺ which can be deduced from a qualitative curve shape comparison of all three mass numbers. The peak area integration for $m/z=19$ yields 0.0044 E–7 A·s for the first peak (base line not shown for better legibility) and 0.11 E–7 A·s for the broad one, which gives 0.003 and 0.07 mg HF, respectively.

It was now attempted to apply this presumably more reliable calibration factor to the evaluation of the TA–MS curves of the same series of fluorides. It has been established that the 10-times smaller calibration factor yields mass losses for HF which approximate the values found by TG. This can be illustrated by the example of Na₃AlF₆·0.6H₂O (Fig. 6). Here, a three-step dehydration range (60–350 °C) with a slight HF evolution during the second one is followed by a broad temperature range where

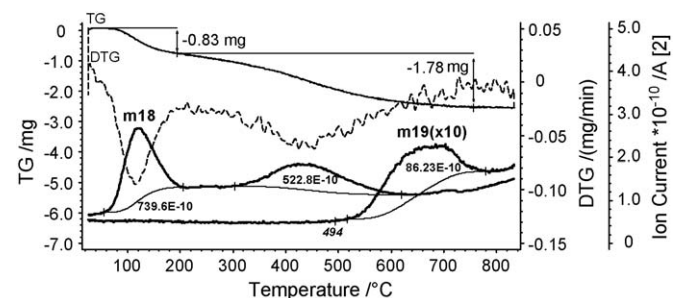


Fig. 7. TA–MS curves of AlF_{2.6}(OH)_{0.4}·0.12H₂O together with the peak area integration for water and HF. Note the increased IC level between the two water peaks. Even a partial peak area integration procedure cannot reliably take into account this additional water amount. Consequently, all obtained water values are too low.

Table 1

Comparison of the mass losses obtained by TG and by quantitative evaluation of MS signals (to Figs. 6 and 7)

Substance	Δm_{TG} (mg)	Δm_{MS} (mg)	Diff. (%)
$\text{Na}_3\text{AlF}_6 \cdot 0.6\text{H}_2\text{O}$	Δm_1 (45...360 °C) = 0.96	$m_{\text{H}_2\text{O}} = 0.30$	-69
	Δm_2 (360...825 °C) = 0.12	$m_{\text{HF}} = 0.07$	-42
$\text{AlF}_2.6(\text{OH})_{0.4} \cdot 0.12\text{H}_2\text{O}$	Δm_1 (47...194 °C) = 0.83	$m_{\text{H}_2\text{O}} = 0.56$	-33
	Δm_2 (194...756 °C) = 1.78	$m_{\text{H}_2\text{O}+\text{HF}} = 0.45$	-75

only HF is released². The mass loss obtained by evaluation of the $m/z = 19$ signal amounts to 0.07 mg and is comparable to the TG value of 0.12 mg. This is the typical order of magnitude for pyrohydrolysis and is close to the determination limit of this type of thermobalances.

The compound $\text{AlF}_2.6(\text{OH})_{0.4} \cdot 0.12\text{H}_2\text{O}$, adopting the HTB structure type, behaves slightly differing. The TG–MS curves in Fig. 7 show a greater mass loss in the high-temperature range with a partially overlapping release of H_2O and HF.

A comparison of the mass losses determined by TG and by quantification of the MS signals $m/z = 18, 19$ (Table 1) shows that the values for HF obtained with the new calibration factor are more realistic as they are generally low. But, unfortunately, a really satisfying quantitative description cannot be drawn, as the determination of the peak area remains uncertain, i.e. too low for correctly representing the liberated water amount.

If one takes into account that the water determination itself by quantifying the signal $m/z = 18$ usually gives excellent results³ it becomes obvious that the problems arise for compounds with a more or less simultaneous release of H_2O and HF.

Two interpretations, closely related, seemed obvious to us: either the qualitative curvature for the $m/z = 19$ does not reliably reflect the HF evolution from the sample and/or the measuring cell. This is illustrated by a typical feature in Fig. 7, where the well-expressed maximum for $m/z = 19$ has no corresponding TG effect. The second interpretation might be that the retention of HF due to adsorption together with a low reproducibility is so strong that no reliable interpretation can be drawn. We tried, therefore, to obtain a direct experimental description of the hydrolysis behaviour of metal halides by constraining it via direct water injection into the purge gas stream.

3.3. Pyrohydrolysis of metal halides by injecting liquid water

For this purpose, the PTA technique is quite appropriate. Fig. 8 demonstrates that chromium(III) chloride, which does not tend to hydrolyse too strongly, immediately produces HCl if 1 or 5 μl $\text{H}_2\text{O}(\text{l})$ were injected in the preheated (110 °C) purge gas stream at 350 or 490 °C, respectively. It is characterized by the mass number $m/z = 36$ (HCl^+) which is detected simultane-

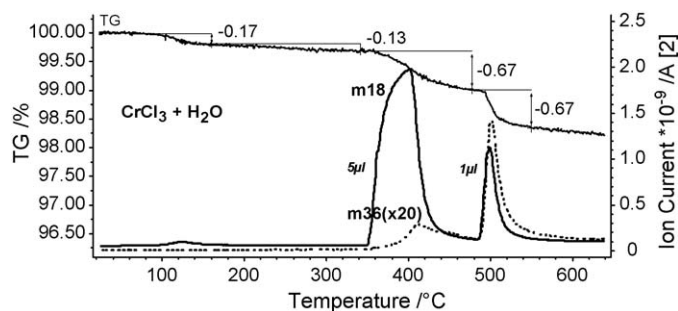


Fig. 8. PTA curves of CrCl_3 . The IC curve for $m/z = 18(\text{H}_2\text{O}^+)$ shows a small dehydration peak above 100 °C followed by the water injection pulses affecting the HCl mass losses.

ously with the water signal. It is noteworthy that a temperature of 380–400 °C is not sufficient for constraining a vivid hydrolysis reaction whereas at 500 °C, as expected, the signal for HCl is sharp and intense.

We applied now the same procedure to two fluorides, one of them being rather sensitive against hydrolysis (FeF_3), the second one rather inactive (MgF_2). In order to further reduce the hydrolysis tendency of the MgF_2 we choose a freshly mortared single crystal of MgF_2 as sample to be investigated.

One of the basic problems in the given concern is that practically each fluoride more or less tends to hydrolyse if the temperature is high enough. This means that we cannot differentiate by means of TA–MS between slight pyrohydrolysis and its complete absence which, on the other hand, would much facilitate a comprehensive quantitative understanding of the pyrohydrolysis degree by quantifying MS signals.

Figs. 9 and 10 illustrate that the behaviour of FeF_3 and MgF_2 is quite different from that of CrCl_3 but also different among each other. Unfortunately, the case of MgF_2 cannot be regarded as the case of complete absence of pyrohydrolysis, even if the degree is

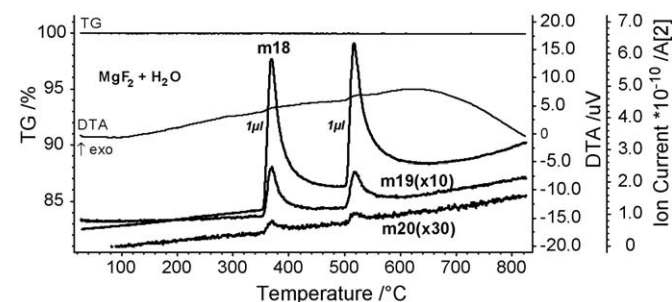


Fig. 9. PTA curves of MgF_2 (powdered single crystal, pretreated in nitrogen up to 500 °C, 1 μl $\text{H}_2\text{O}(\text{l})$ injected) as an example for very weak pyrohydrolysis. Note the absence of increasing intensity for $m/z = 19$ and 20 at higher temperatures.

² The increasing IC intensity for $m/z = 18$ above 500 °C does not indicate a water release but is due to the constructive design of the Skinner apparatus, where the MS signals are temperature-dependent (cf. footnote 1)

³ The value for the water amount found for the dehydration of $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ exceeds the TG value by only 0.9 %.

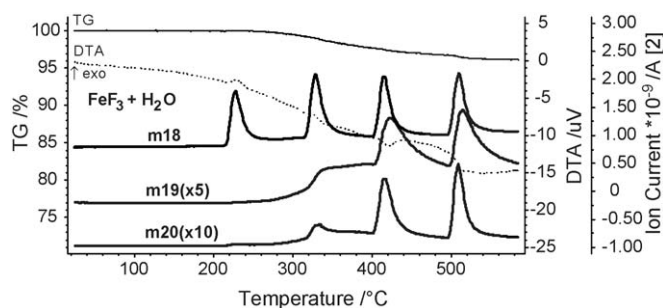


Fig. 10. PTA curves of $\text{FeF}_3 \cdot n\text{H}_2\text{O}$ ($1 \mu\text{l H}_2\text{O(l)}$ injected), an example for a substance with greater hydrolysis tendency. Bigger amounts of HF than shown in Fig. 9 have been formed. The underlying mass loss above 250°C is due to continuing dehydration (the sample was preheated up to 250°C only).

especially low. The observed intensity ratio of the mass numbers 18:19:20 = 105:4:1 deviates from the expected one (ca. 500:1:1) due to a certain contribution to $m/z=19$ caused by HF. But, undoubtedly, this example can be considered as the minimum case of hydrolysis tendency.

The behaviour of FeF_3 remarkably differs from that of the fluoroaluminates (cf. Figs. 6 and 7) where the immediate detection of low (!) quantities of HF was hindered by strong adsorption in the apparatus. The case of FeF_3 in Fig. 10 proves, however, that it is not impossible to detect more or less simultaneously the HF evolution which occurs under these conditions: the absolute quantity of HF must be considerably higher. The same is true, e.g. for fluorides such as $\text{NaHF}_2 \cdot n\text{H}_2\text{O}$ or $\text{NH}_4\text{HF} \cdot n\text{H}_2\text{O}$ (not shown here) where strongly deviating intensity ratios for the related mass numbers 18, 19, and 20 were observed. The curve shape for FeF_3 , however, is not appropriate for a reliable surface evaluation of the $m/z=19$ which relates primarily to the strong tailing thus avoiding a correct base line drawing.

4. Discussion

Trying to summarize this rather complicated situation one should point out the following. On the one hand, there are experimental data allowing for an approximating interpretation based both on mass loss values and on the temperatures and the maxima of the $m/z=19$ signal. This is possible if the calibration of the mass number 19 has been performed by direct liquid injection as described by Maciejewski [13] taking into account that steady state conditions for the evaporation of azeotropic systems must be reached.

But these conditions are practically never fulfilled when fluorides hydrolyse or fluoride-hydrates decompose. Not the HF determination seems to be the crucial problem but the interaction of water and HF—as in the surface/bulk of the thermally treated compound as in the gas phase after desorption from a solid surface whatever this surface might be (i.e. either the decomposing solid or a sorbent such as apparatus parts).

The solid sample and its adsorption properties are of special importance if one deals with various aluminium fluorides. In an earlier paper we could show that AlF_3 is a stronger Lewis acid

than chromium(III) salts or FeF_3 [17]. For this reason, these compounds were no longer applied as catalysts in the synthesis of chlorofluorocarbon (CFC) alternatives in industry. This is in good accordance with the recent finding that, after Au(V) and Sb(V), Al(III) adopts the highest fluoride ion affinity known up to now [18]. This can explain that the water and HF determination primarily fails in the case of aluminium fluorides and/or aluminium hydroxo fluorides as the retention both of H_2O and HF is especially strong.

The interaction H_2O –HF drastically lowers the water amounts detected in the MS which leads to the unsatisfying situation that a reliable quantitative interpretation is often, but not always impossible. The interaction H_2O –HF yields H_3O^+ and F^- both adopting the mass number $m/z=19$. Both species are strongly adsorbed at solid surfaces which can even lead to the extreme situation that practically no intensity for $m/z=19$ is registered in the MS (e.g. observed for $\alpha\text{-AlF}_3$).

Furthermore, there are numerous examples, where IC intensities for $m/z=19$ are detected but no corresponding mass loss is registered. This can be explained by the known greater sensitivity of the MS compared with that of TG. This is of special importance if small quantities of HF have to be followed. Together with the bad reproducibility of the HF retention behaviour this might affect the impression that the HF evolution itself is appearing only. And, finally, the probably high ionization probability for the $m/z=19$ has to be taken into account as complicating influence factor. For the water mass numbers 17 and 18, this ionization probability is known to be especially high, but it is not known both for $m/z=19$ (F^+) and 20 (HF^+ , $\text{H}_2^{18}\text{O}^+$). Consequently, their influence on the IC signals remains uncertain.

5. Conclusions

It has been shown that the differential calibration method by using direct liquid injection yields reliable calibration factors both for H_2O and for HF. In most cases, the evolution behaviour of HF alone is correctly reflected as the calibration method yields absolute quantities being 10-times smaller than do other methods. This is in good accordance with the observation that well-expressed IC signals for $m/z=19$, representing HF, in fact represent very low masses of HF which normally cannot be followed by TG analysis. The values for water, which can be obtained by PTA evaluation, remain rather uncertain if H_2O and HF are released more or less simultaneously. This is a consequence of the extreme interaction intensity between both molecules and is further complicated as the system H_2O –HF is azeotropic.

One is facing, therefore, the rather curious situation that the TA apparatus can be calibrated reliably both for water itself and hydrogen fluoride itself, but a joint application of both calibration factors to a comprehensive quantitative description of the thermal behaviour of a fluoride is almost failing. This is a consequence of the extreme chemical properties of fluorides and/or fluoride hydrates which behave in a very complex and complicated manner.

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References

- [1] M. Maciejewski, C.A. Müller, R. Tschan, W.-D. Emmerich, A. Baiker, *Thermochim. Acta* 295 (1997) 167.
- [2] M. Maciejewski, A. Baiker, *Thermochim. Acta* 295 (1997) 95.
- [3] M. Maciejewski, A. Baiker, E. Kapsch, M. Hollering, W.-D. Emmerich, *GIT Labor-Fachzeitschrift* (06/2001) 616.
- [4] F. Eigenmann, M. Maciejewski, A. Baiker, *Thermochim. Acta* 6276 (2000) 1.
- [5] M. Feist, Th. Krahl, E. Kemnitz, Proceedings of the 13th European Symposium on Fluorine Chemistry, Bordeaux, France, July 15–20, 2001, p. B21.
- [6] E. Post, et al., Coupling Techniques in Thermal Analysis, in: Proceedings of the 4th Selber Kopplungstage, Selb, Germany, June 24–26, 2001.
- [7] G. Scholz, R. Stösser, Ch. Legein, J.Y. Buzaré, G. Silly, *Appl. Magn. Reson.* 18 (2000) 199.
- [8] D.-H. Menz, *J. Therm. Anal.* 38 (1992) 321.
- [9] M. Ahrens, G. Scholz, M. Feist, E. Kemnitz, *Solid State Sci.* (2006), in press.
- [10] D. Dambournet, A. Tressaud, M. Feist, A. Demourgues, in preparation.
- [11] W.-D. Emmerich, E. Post, *J. Therm. Anal.* 49 (1997) 1007.
- [12] E. Kaisersberger, E. Post, *Thermochim. Acta* 295 (1997) 73.
- [13] F. Eigenmann, M. Maciejewski, A. Baiker, *Thermochim. Acta* 440 (1) (2006) 81.
- [14] F. Barontini, E. Brunazzi, V. Cozzani, *Thermochim. Acta* 389 (2002) 95.
- [15] A. Galindo, P.J. Whitehead, G. Jackson, A.N. Burgess, *J. Phys. Chem. B* 101 (1997) 2082.
- [16] D. Babel, A. Tressaud, Crystal chemistry of fluorides, in: P. Hagemuller (Ed.), *Inorganic Solid Fluorides*, Academic Press, 1985, p. 77.
- [17] E. Kemnitz, J.M. Winfield, in: T. Nakajima, A. Tressaud, B. Zemva (Eds.), *Advanced Inorganic Fluorides: Synthesis, Characterization and Applications*, Elsevier Science, SA, 2000, pp. 367–402.
- [18] K.O. Christe, D.A. Dixon, D. McLemore, W.W. Wilson, J.A. Sheehy, J.A. Boatz, *J. Fluorine Chem.* 101 (2000) 157.