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History of one discovery
Collaboration was difficult but rewarding

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1. Introduction

After the appearance of commercial electrothermal (ET) atomic absorption spectrometry (AAS) equipment in 1970, many analytical laboratories initiated studies on the features of sample atomization in relation to the experimental conditions: temperature and heating rate, flow of the internal purge gas, dimensions and shape of graphite tubes, presence of a matrix modifier, etc. This interest was associated in part with an optimization of analysis conditions and in part with attempts to interpret the mechanisms and kinetics of vaporization of solid substances. Different spectrometry techniques were applied.

2. Mass-spectrometry studies

In the 1980s, quadrupole mass spectrometry (QMS) was used for the first time for these purposes [1–5]. In most cases [2–5], the objects under investigation were solutions of metal nitrates. The main goal of these experiments was to elucidate the mechanism of the pyrolysis of these salts in the stage of low-temperature heat treatment, preceding the atomization of the sample residue. Experiments were performed in a high vacuum. The sample was placed on a miniature graphite platform under the quadrupole analyzer. Studies performed by Sturgeon et al. [2] with lead nitrate revealed for the first time the release of PbO molecules into the gas phase at 550 K. This unexpected effect was later confirmed by Holcombe et al., who observed oxide molecules in the gas phase in the pyrolysis of Pb, Ni, and Cu nitrates at 550 [3], 625 [4], and 340 K [5], respectively.

The appearance of the oxide molecules in the gas phase was attributed in [3–5] to their “mechanical detachment” by gaseous products (NO_2 and O_2) in the course of crystal destruction or by the desorption of separate oxide molecules that appeared on the graphite surface upon solvent evaporation. Both these hypotheses, in my opinion, had no reliable theoretical grounds and were in disagreement with the actual observations. The “mechanical” hypothesis was inconsistent with the smooth variation of the signal, typical of equilibrium vaporization, while the “desorption” hypothesis, with the fact that the main part of the sample (several micrograms in mass) was in the form of crystals clearly observable under a microscope.

3. Collaboration

After thorough analysis of these results, I put forward the hypothesis of the congruent dissociative vaporization (CDV) of metal nitrates with simultaneous condensation of low-volatility products [6,7]. It is remarkable that the major arguments in favor of this mechanism were the results reported just by Holcombe et al. [3–5]. Upon heating $Pb(NO_3)_2$ and $Ni(NO_3)_2$ up to their complete vaporization, two peaks were observed in the recording patterns of each of these substances. The first peak (PbO^+ or NiO^+) corresponded to the decomposition of the salts, and the second peak (Pb^+ or Ni^+), to the dissociative vaporization of the oxides PbO and NiO (see a typical diagram on Fig. 1). The areas of the low- and high-temperature peaks are approximately equal. This implies that the decomposition of the salt (the first peak) proceeds in a congruent way, with half of the metal oxide vapors, as should be expected from geometric considerations, condensing on the flat heater surface.

It should be noted that the choice of nitrate salts as objects for QMS study, fortunately, was the only acceptable way to detect the low-volatile products in the gas phase. The point that the nitrates for many metals have low melting points and are volatilized as melts. Unlike solid salts, the surface of melts is free of layers of solid products, which limit the entry of low-volatile molecules into QMS. In the case of decomposition of high-melting compounds (e.g., sulfates or phosphates) the low-volatile molecules condense in the solid product shell and their observation is impossible.

Unfortunately, all my arguments did not convince Jim. After long discussions during our meeting at the 1991 Pittsburg Conference in Chicago, we decided to carry out additional (more thorough) experiments on the thermal decomposition of silver, cadmium, lead, and copper nitrate. Using Jim Holcombe's invitation and the support of the US National Science Foundation, I sent to Holcombe's laboratory my postgraduate student, Alexander Novichikhin. After 4 months of intensive work (summer 1993), Alexander returned home with a heap of results obtained and… with the confidence that Holcombe's opinion is right.

I was not discouraged by this fact, because I knew well how strongly Jim defends his opinion. A scrupulous quantitative analysis of the data obtained showed that thermal decomposition of Ag, Cd, and Pb nitrates occurred congruently and that the main kinetic parameter E for the decomposition processes was in good agreement with the enthalpy values calculated for the dissociative vaporization of these compounds. Nevertheless, the version of a joint article that I prepared for *Spectrochimica Acta Part B* (*SAB*) was flatly rejected by Holcombe, and our fierce debates resumed.

I cite as an example a copy of one of my letters to Jim (FAX from St Petersburg, February 4, 1994): “Dear Jim, We agree, in principle, with your idea to make an attempt at composing a MS that might be mutually acceptable but, to tell the truth, now we are not sure in its realizations. Our antipodal positions in the interpretation of the phenomena are important but not the main reason of the failure on this way. More important that you and your colleagues do not want to understand and accept

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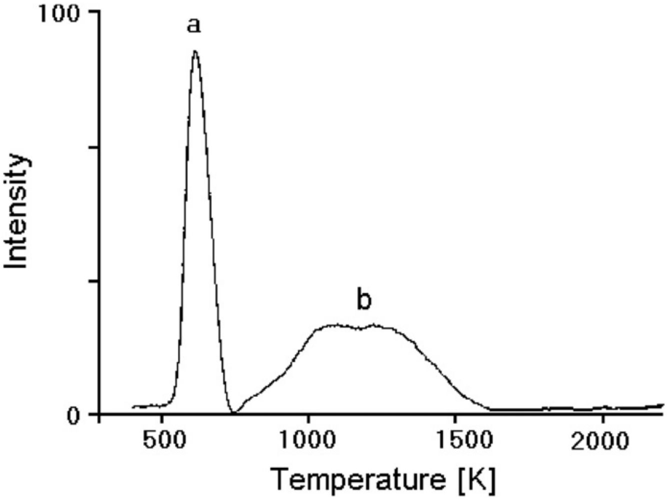

Fig. 1. Mass intensity signals of Pb-species for the thermal decomposition of lead nitrate sample containing 0.4 μg Pb at heating rate 600 K s^{-1}: (a) PbO^+ and (b) Pb^+ [3].

some of our ideas, explanations and proposals. (We cannot understand the reason. May be, it is because of our poor English?) Let us illustrate this conclusion by two examples… (*Two pages of this letter with my proposals are omitted here*).

You should agree that for 7 months of our debates (from July 1993) you could not find any serious arguments against the gasification theory and could not prove or even support your crystal shattering (now expulsion) hypothesis. That is why, we propose now to submit the MS in its original form (after some editorial and linguistic improvements). If you find some arguments against the gasification theory during 2–3 months, you can delete your names in the MS and prepare for publication some critical notes. That is exactly the same you proposed me in your letter of August 4. Of course, we do not mind if you submit your original (or improved) version of the MS simultaneously with ours. It might be interesting for some people involved in this problem. But, as for us, we prefer to have a joint publication. Waiting for your response. Sincerely yours, Boris and Sasha".

The story lasted more than one and a half years and ended with the "Solomon's decision" of Walter Slavin, which was at that time the Editor-in-Chief of the journal, to simultaneously publish separate papers written by each "party." As a result, the *SAB* issue of October 1995 contained four papers (two from each party) containing a description of the experiments and an interpretation of the results [8–11]. The authors' standings remained unchanged.

It is noteworthy that our relationships, outside of debates on several mechanistic problems, were always very friendly. On invitation of Jim, I visited Austin University (Fig. 2) and spent a wonderful week staying in his house. Jim has kindly organized through the US National Science Foundation sending to my Department in St Petersburg University some office techniques (Dell PC and Xerox 5310). This was very valuable support for my lab at the heavy 90s in Russia.

Despite satisfaction with the results obtained, I realized that further development of this project on the base of ET AAS and QMS is limited by insufficient precision and accuracy of these methods, by the small masses and unusual shape of solid samples (residues after drying of solutions). A need to look for other research means arose… The correct choice of the field of physical chemistry and of the technology associated with studies of solid-state decompositions was obvious. Thermochemistry and thermal analysis (TA) were most suitable for this purpose.

4. Thermogravimetric studies

Previously I had no experience in the theory and practice of TA. However, by a lucky coincidence, I had gradually collected for my home library the literature on thermochemistry, including handbooks on thermal constants and thermodynamic properties of substances. Thus, I was prepared for work with the published data and for its critical analysis. In the beginning of 1996, I started systematic work on the preparation of reviews on problems that seemed topical to me. Ultimately 11 articles have been published in *Thermochimica Acta* during the next four years. Only in 2001, I met a qualified specialist in TA, Dr Valery Ugolkov (Institute of Silicate Chemistry, St Petersburg) who readily agreed to collaborate and to verify experimentally the unusual theoretical ideas put forward by me. Our collaboration has been very fruitful and resulted in the publication of 15 joint papers.

Fig. 2. During my visit to the Texas University in Austin in March 1991.

To summarize, the last 25 years of my scientific career were mainly devoted to studying this problem. The results of this work were presented in more than 70 regular articles and reviews published in *Spectrochimica Acta Part B*; *Thermochimica Acta*; *Journal of Thermal Analysis and Calorimetry*; *Microchimica Acta*; *Journal of Analytical Chemistry*; *Russian Journal of Applied Chemistry*; *Reaction Kinetics*, *Mechanism and Catalysis*; *International Reviews in Physical Chemistry*, and in a book [12] where the results of all my previous articles (published before 2007) were summarized.

Taking into account the data presented in our recent publications [13–29] the major results obtained during the whole 25-year period might be presented by the simplified scheme (Fig. 3). As can be seen from this scheme, the thermochemical model (approach or platform) includes three independent constituents: the CDV mechanism, as the main component, and two others, the Langmuir vaporization kinetics and the third-law method of *E* determination, as additional components. The theory is based on fundamental concepts of molecular physics and chemical thermodynamics. Ultimately, creation of this thermochemical model may be considered as an important contribution of electrothermal AAS and QMS, and also TA, into heterogeneous chemical