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# From a physicist's toy to an indispensable analytical tool in many fields of science
## A personal view of the leading contribution of Ondrej Krivanek to the spectacular successes of EELS spectroscopy in the electron microscope

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A B S T R A C T

This contribution aims at reporting, from the subjective point of view of a witness based in Orsay, the fundamental role of Ondrej Krivanek in the spectacular emergence of EELS (Electron Energy-Loss Spectroscopy) as a key tool in analytical electron microscopy. In this regard, he has successively designed and built while he was at Gatan, serial EELS spectrometers, parallel EELS spectrometers and post-column energy filters which have been fitted to many different (S)TEM columns installed around the world. More recently the implementation of monochromators on the NION dedicated STEM together with the realization and performance of aberration correctors (which lie out of the scope of the present review), have placed the most advanced instrumental tool in the hands of continuously increasing populations of users in many domains of materials science and in life sciences. Furthermore, the impact of Ondrej Krivanek has spread widely beyond his technical achievements into that of a highly respected organizer of workshops, bringing together at regular intervals, all the experts from around the world and building up a real community of scientists.

## 1. Introduction

One day, at the end of July 1978, Ondrej Krivanek and myself first met, during a specialist workshop in Analytical Electron Microscopy (AEM), held at Cornell University. This was the second workshop of this name; the first one two years earlier, had beautifully introduced and promoted the general concept and the practical aspects of AEM. In this context, spectroscopy tools added onto the column of a transmission electron microscope (TEM) constitute useful components which enlarge its domain of exploration by providing local information on the chemistry as well as on the electronic properties of the specimen. By the way, two papers published a couple of years before in the first issue of the journal Ultramicroscopy had firmly established the fundamentals and the perspectives of the EELS technique in a TEM. The first one by Isaacson and Johnson [1] had focused on the use of EELS for the microanalysis of light elements, evaluating the two important parameters to be improved, the Minimum Detectable Mass (MDM) and the Minimum Detectable Mass Fraction (MMF), and concluding after a first round of preliminary experiments that “the feasibility of elemental analysis of single light atoms remains a distinct possibility (in theory, at least!)”. On their side, Colliex et al. [2] had more extensively described the richness of the information contained in an EELS spectrum recorded in the transmission mode from a nm-sized area and revisited the influence of various parameters in the drive towards the ultimate detection limits using this technique. I however confess that the use of the word “ancillary” in the first sentence of the conclusion of this paper “Electron energy loss spectroscopy must be regarded as a very promising ancillary method in electron microscopy”, does not sound today very optimistic, when reading it!! I want to point out at this stage, that both papers were mentioning the development and introduction of parallel detection devices as an anticipated necessary step to come closer to the identification of the individual atom.

It is therefore no surprise that the EELS technique was in 1978 at the center of heated debates concerning the future of AEM. Therefore, the young Ondrej Krivanek came to me and asked: “Christian what do you think of the future of EELS?”. Listening to his own report of the ensuing exchange, it now appears that I did not show a great deal of optimism, diverting the discussion toward other subjects (liquid metal ion sources, contrast of inelastic images of phase objects…) which I was exploring at the same time with my first students, Pierre Sudraud and Claudie Mory. I feel that I may have masked a bit that a third student, Pierre Trebbia, was very much involved at that time in the introduction and use of computer control and analysis to progress towards quantitative processing of EELS data. Revisiting now my own blurred

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memories, maybe I had felt that if such a young and bright guy, Ondrej, had immediately entered this field, the competition would quickly have become very severe. You all know, now, what happened: the rest of this paper will emphasize the major inputs, realizations and successes in the field of EELS in a (S)TEM, which have to be unambiguously attributed to Ondrej Krivanek and which the many different contributions to the present Ultramicroscopy issue beautifully illustrate today, i.e. 40 years after the beginning of my story here above. I can also recommend to interested readers the TEM-EELS personal perspective by Ray Egerton, published a few years ago in a previous issue of Ultramicroscopy [3].

## 2. The first generation of Gatan serial EELS

As a matter of fact, the sixties and early seventies had been rich with instrumental developments of energy analyzers and filters (magnetic sectors, combined magnetic sectors-electrostatic mirrors, Wien filters) either introduced in the middle or at the bottom of the TEM column. These systems, all made through local initiatives in research laboratories (Chicago, Orsay, Oxford, Cambridge, Cornell), had generated an initial output of fundamental physical studies, such as the excitation spectra of nucleic acid bases [4,5], the fine structures on core losses in different materials including solidified rare gases [6,7], the dispersion curves E(k) of plasmons and Cerenkov losses [8] in thin metallic and semiconducting films. But, it could be pointed out that no such attachment was commercially available for TEMs, except a first design of an EELS magnetic sector on top (i.e. at the end of the electron trajectories) of the newly built VG HB5 dedicated STEM microscope, the first versions of which had been installed in London and Cambridge in the mid 70 s. Obviously, this domain constituted at that time a potentially rich market.

Let us come back to Ondrej's start in EELS in 1978 after the Cornell workshop, a description of which can be found in his own account published in the Proceedings of the IFSM meeting in Prague 2014 [9], when he was awarded the IFSM Cosslett medal. Back at the Lawrence Berkeley National Lab where he was employed at that time, he convinced his boss, Gareth Thomas, to give him the modest support required to build his first spectrometer described in an EMSA abstract in 1979, and producing spectra over large energy ranges (from zero to 2000 eV) at about 2 eV resolution, see Fig. 3 in [9]. This was quite an encouraging achievement. He was quickly approached by Peter Swann, head of the young Gatan enterprise, and they designed together the mark II, which became the Gatan 607 serial EELS, described in [10]. By this time, he had moved to ASU as Associate Director of the HREM facility, where Fig. 1 shows him at work in his office and outside in the Arizona environment. His long and fruitful connection with the Gatan company had started in parallel, where he later became Director of Research.

The year 1981 was particularly rich in results issuing from ASU, with four papers at the EMSA meeting and one at the EMAG conference, and also from Orsay with three papers at the EMAG conference. The work performed at ASU was mainly focused on the retrieval of crystallographic information and on the role of orientation, giving rise to channeling and blocking effects. It also resulted a little later in the famous EELS Atlas, the reference guide of electron energy loss spectra covering all stable elements, jointly published by ASU HREM Facility and Gatan Inc. [11]. I can testify that I have myself been an addict of this Atlas which was always accessible on the microscope control table while I was recording spectra.

Ondrej came and spent three months in Orsay during spring 1981. We had acquired a few months earlier one of the first HB 501 dedicated STEM VG microscopes and we were on the verge of pushing this bright new machine into the exploration of its analytical performance capacities, the first of which was obviously that associated with EELS spectroscopy. Ondrej had brought a prototype of the EELS 607 spectrometer, which immediately demonstrated much higher performance than the original VG spectrometer [12] and this became our work instrument until it was sent to retirement with the arrival of the second generation of Gatan spectrometers, i.e. the parallel detection system. As a matter of fact, the 607 serial Gatan spectrometer benefited from an efficient correction second order aberrations due to an improved design of its pole pieces as well as a better optical coupling, leading to better transmissivity. At this time, with a probe of 0.5 nm, the signal-to-noise ratio was sufficiently good to record core-loss spectra (i.e. Ca $L_{23}$) with a 1 eV energy resolution, while the FWHM of the zero loss peak was of the order of 0.4 eV. Early applications involved spectra and energy-filtered images of uranium clusters on thin foils of carbon and of Si-$SiO_2$ interfaces [13]. Through these studies, the association of a STEM fitted with a field emission gun (FEG) of high brightness capable of delivering a current of a few pA to hundreds of pA in a sub-nm probe, with a suitably adapted and corrected EELS spectrometer, had clearly been demonstrated to constitute an excellent way of exploring the use of electron spectroscopy in materials with the best performance then available.

Let us move to the year 1988, when Mike Isaacson and myself managed to obtain from our agencies, NSF in the USA and CNRS in France, the financial support for the organization of a workshop at Aussois in the French Alps during winter, which would be "in effect" a third Cornell meeting, ten years after the second one. This new workshop, devoted to "nanometer-scale electron microscopy", provided an evaluation of the progress and successes obtained over the previous decade, mostly but not uniquely when applied to materials science. The proceedings of this workshop, gathered in a single Ultramicroscopy issue [14] are very rich in illuminating contributions, interlaced with summaries and conclusions. As regards EELS in the (S)TEM, the focus at that time was on detection systems and more particularly on parallel EELS. It was not a surprise, as such an upgrade had been firmly recommended more than ten years before [1,2]. As noted by A. Eades [15] in his summary of the session on one- and two- dimensional electron detectors encompassing the description and discussion of six parallel EELS detection systems, "the revolution observed in electron detection is brought in part by the development and incorporation into electron microscopy of CCDs and PDAs, and in part by the advances in computing and digital storage, that have made it possible to acquire and process large numbers of images in digital format". In his own contribution to this workshop proceedings, Krivanek describes improvements which he has brought to the Gatan parallel EELS spectrometer under development [16]. Fig. 2, recorded during this meeting, shows the high density of (S)TEM-EELS experts gathered in the sunny French Alps, where our ski champion, Ondrej Krivanek, keen to mention in his wikipedia list of awards his "1st places in special and parallel slaloms at the 1975 Oxford-Cambridge Varsity ski race", could fully demonstrate his skills on the steep slopes.

## 3. The Gatan parallel EELS system and the subsequent EELS spectrum-imaging era

As a matter of fact, the presentations on parallel EELS detection in Aussois stemmed from a flourishing context of previous studies. As early as in 1981, with the target of pushing down the detection limit for a trace element (typically Ca) in a biological tissue, Shuman had tested the implementation, pros and cons, of photodiode arrays either under direct electron exposure or with the introduction of light-conversion systems [17]. Using a light-coupling design together with a multiple-element photon detector, Shuman together with Kruit [18], then with Somlyo [19], developed the necessary routine to process the so-acquired low signal-to-background spectra and to extract quantitative measurements of weak concentrations. On their own side, Krivanek and colleagues at Gatan [20], had also undertaken the installation and test of a parallel detection system, made of a three-quadrupole magnification unit delivering variable ranges of energy-loss electron distributions on the parallel EELS detector. This latter was made of a