

The Legacy of Raimond Castaing

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Abstract. In April 1998 Raimond Castaing left the world of electrons, of ions and others particles, his wife and his family, his numerous students, for the world of stars.

Raimond Castaing (Fig. 1) had a very strong personality. No one will forget their first meeting with him and all his students remember how brilliant he was as a teacher. A lot of anecdotes about his famous hot temper are still circulating among his friends and his former students. But in this paper, we would like to evoke Castaing's memory through his achievements in Instrumental Physics, from the time of his doctoral thesis to later developments with his students, which were all centred on the imaging of the microstructures of materials and their quantitative chemical analysis.

Key words: History; Castaing's microprobe; EPMA; SIMS.

Castaing's Electron Probe Microanalyser

It is worth relating in some detail the story of the birth of the Castaing electron probe microanalyser, as it is quite instructive. As a graduate in Physics, Raimond Castaing entered the Institute for Aeronautical Research (ONERA), which had been recently created by the French government, in January 1947. In the Materials Science department, he was very lucky to be endowed with two electron microscopes, very exceptional equipment – a real luxury – in 1948. The first one, an American RCA instrument was devoted to metallurgical studies, especially to precipitation in aluminium–copper alloys. This was a favourite field of Professor André Guinier who discovered, just on the eve of the second world war, the origin of the

hardening of these alloys which is due to small copper clusters that produce typical diffusion patterns in X-rays diffractograms, the now well known GP (Guinier-Preston) zones. The hope of Guinier and later the ambition of Castaing was to observe these mysterious zones in real space thanks to this new microscope.

It was during a conversation mostly devoted to the microstructure of Al-4%Cu alloys, with their various precipitates, θ , θ' and θ'' , and the famous GP zones, that Guinier questioned Castaing about the possibility of performing local (point) analysis by bombarding an alloy specimen with electrons, detecting the characteristic X-rays emitted and by applying Moseley's law, identifying the elements present. Guinier was an expert in X-ray diffractometers with specially cut and ground quartz crystals, but he appealed to Castaing's opinion about the feasibility of such an experiment. Let us quote Castaing himself: "I replied straightaway that to my mind it was very easy to do and it was surprising that no one had done it before". We can only wonder at the real difficulties he had to face.

Some preliminary experiments with a conventional X-ray tube, a curved crystal monochromator and a Geiger counter, made Castaing change his opinion. A few pulses per minute would not allow any analysis, not even a qualitative one. This conclusion was too pessimistic, as a broad source of X-rays was not well matched to a focusing spectrometer. Results would be better with a point source. Therefore, the problem Castaing had to resolve was how to obtain a fine beam of electrons. The second microscope he received, built by a French company (Compagnie Française de Télégraphie Sans Fils, CSF), seemed to be a gift specially dedicated for this purpose. It was a machine working with electrostatic lenses, which he didn't

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Fig. 1. Raimond Castaing

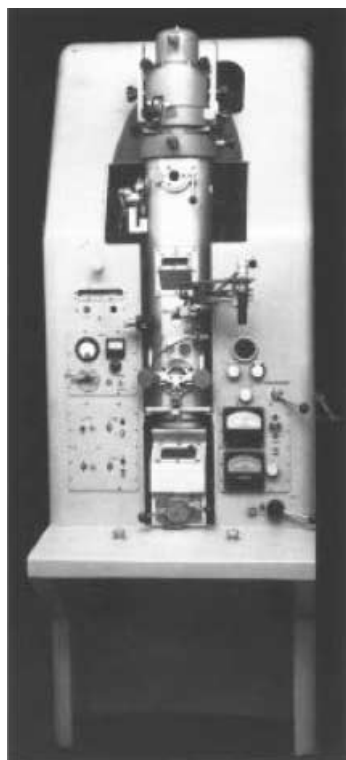


Fig. 2. The first electron microprobe (from Castaing's thesis)

hesitate to cannibalise in order to produce the required fine electron beam, though not without a lot of practical difficulties (Fig. 2). He had soon to face many physical problems, which made him understand why

probably others had failed. Lens aberrations had to be corrected to produce an intense, fine beam of electrons. Certainly there were excellent books describing the lens aberrations (Zworykin's especially), but these did not give any warning about dust particles, grease layers, and so on... that scatter the electron beam.

Let us quote again Castaing: "By the beginning of 1949, I had succeeded in injecting into a probe of about one micrometer a current of a few thousandths of a microampere, and of this I was very proud. Sure enough there were papers in which people claimed to have produced probes of two hundreds Angströms, but I was not far from thinking they were out-and-out liars..." [1].

Another problem relating to X-ray detection soon arose. It was easy to detect the continuous background, but not very informative. Finally Guinier lent Castaing one of his precious quartz crystals (specially cut and ground, of the Johansson type). It was fitted in a small spectrograph (Fig. 3) that was attached to the outside of the main column. In the first days of 1949, he was able to measure the characteristic X-emission from a 1 μm , 4 nA, electron probe. Considering the poor conditions in France after a terrible war, the rapidity with which this result was obtained was quite remarkable.

This result was presented in July 1949 in Delft (the Netherlands) during the first European Conference on Electron Microscopy [2]. According to the proceedings, a part of the discussion focused on the limited resolution due to the diffuse scattering of electrons in the specimen. Castaing explained later how he was so discouraged when he heard of the Thomson and Whiddington work which showed that the penetration of the electrons would drastically limit the resolving power of the analysis. That was a dramatic farewell to the study of GP zones!

In 1951, Castaing submitted his Doctor's Thesis at the University of Paris. It was published in a series of ONERA reports [3] and later translated to English by David Wittry. This publication remains a cornerstone in the field and is a must in the scientific literature. It has not aged and reading Castaing's thesis should be recommended to everybody entering the field of microanalysis. All aspects were covered in depth: instrumentation, lens aberrations, optimal probe size, modelling of X-ray emission, the physical basis of the correction calculations, some applications to metallurgy, and even crystallography (Kossel diagrams). We are still speaking of $\varphi(\rho z)$ functions and $f(\chi)$

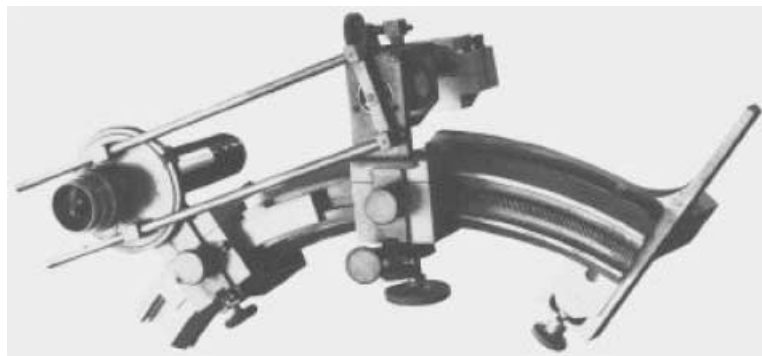


Fig. 3. The curved crystal spectrometer to be fitted to the main column (from Castaing's thesis)

curves. We are still using $\text{cosec}\theta$, although this notation is quite unusual for $1/\sin\theta$. Perhaps the most important idea was the determination of absolute concentrations, thanks to the comparison of the intensities of the same characteristic line of a given element measured on the specimen and on a target made of the same pure element. This approach was radically different from that used in other analytical methods; the empirical calibration curve. Castaing's approach was like a revolution, with a tremendous simplification since all instrumental effects disappear in the intensity ratio. But the other side of the coin was the necessity for a deep understanding of the physical processes involved in the diffuse penetration of the electrons and the emission and absorption of X-rays. Castaing proposed a very clear model for these processes, which after fifty years has not aged.

Professor Guinier thought that things could not remain at this crude stage and that the interest in these first results justified an apparatus being specially designed and constructed – a project that would have been impossible to realise in a university environment, but that should be an excellent challenge for a large and young organisation such as ONERA. Guinier, a wise man, thought that the best solution would lie in the construction of two instruments: one for the inventor (his toy to play with and of course develop for the study of light alloys and other aircraft materials) and one for a metallurgical laboratory that would use it regularly and demonstrate its usefulness and versatility. He easily convinced the French Institute for Steel Research (IRSID), created a few years before by the French steel companies, to take interest in the project and establish a financial agreement. The story looks a little like a fairy tale, as industry people were apparently so easily convinced to put money into a bright and promising, but risky project. What did metallurgists really expect

from such an instrument in the absence of any precise specifications? A few lines from Prof. Guinier were sufficient to convince officials making their decision: “Quantitative analysis is possible, with an accuracy of 1 or 2 % on a mass of material as low as 10^{-11} grams; the analysis is non-destructive. Presently the elements that can be analysed have atomic number above titanium, but in spite of this limitation, the composition of carbides and oxides can be quantitatively determined in iron. Inclusions as small as a few microns can be analysed. The applications of this method that we can muse about are very numerous” [4]. The argument about inclusions was a strong one to persuade steel scientists to come to a positive decision, but that was not sufficient in itself as they were not the ones who held the purse strings! Actually at this time, after the terrible war period, officials had confidence in long-term projects. We are afraid it would be quite different nowadays. Such a project would surely be rejected, or at best submitted to a series of committees.

The construction of two prototypes was only possible with the help of a high level staff, such that ONERA could provide. How patient his assistant Jacques Descamps was, enduring all the day long a hurricane called Raimond Castaing. Castaing was thinking so fast that his colleagues could hardly follow him, and had to ask him if he would please repeat things for their slow minds. That made him still more nervous! Descamps was his clever assistant who succeeded with the measurements of the so useful $\varphi(\rho z)$ curves by the “tracer” technique [5] – so elegant, but so difficult to realise, especially with the limited laboratory facilities of that time – and other small marvels Castaing asked of him as simple services.

Finally, the first instrument (Fig. 4) was publicly presented in July 1955 at the Physics Exhibition, organised every year in Paris by the French Physical

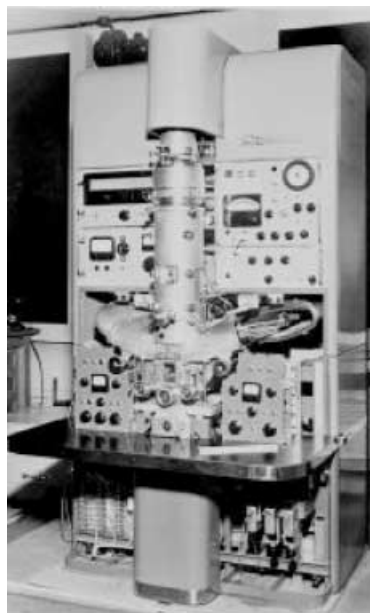


Fig. 4. The Castaing's microprobe prototype

Society. The instrument was not only exhibited, but it was working in the corridors of the old Sorbonne, quite a challenge because of local difficulties with the electric power and the absence of a water supply. The general appearance was that of a nice piece of furniture with the look of an electron microscope of that time. Nevertheless, it was a prototype, without technical documents, guarantees and a maintenance contract, but with all the problems that one of us (J. Ph.) would shortly have to grapple with.

It soon became apparent that for routine quantitative analysis, Castaing's method as developed in his thesis and subsequent papers ought to be changed to a more practical format. On the basis of Castaing's model, one of us (J. Ph.) succeeded in deriving an elegant formula for the absorption correction, that in its simplified form was easy to handle with the tools of that time (slide rule and table of logarithms). This correction formula was presented at the Third International Symposium on X-Ray Optics and Microanalysis in Stanford [6]. It has been used for a long time by a lot of people and was included in several computer software programs.

Looking at this story, we would like to underline the interest people would find in revisiting this period; success and failure remain a source of lessons for our present research activity:

- Post war conditions opened the way to enthusiasm and free research facilities that permitted a blossoming of new ideas. It was not too difficult

to convince officials of the interest of long term (and risky) projects. Why not in present times?

- Castaing opened a new approach to analytical procedures, which remain a model for other analytical techniques. Let us remind ourselves that all analytical methods were based on the use of calibration curves. Nobody had thought previously of the possibility of an absolute analysis.
- To-day more and more metallurgists, materials scientists, biologists and bio-physicians are using sophisticated instruments without a sufficient understanding of the physics involved. This situation can be dangerous and mistakes or wrong interpretations are frequent. The problem is becoming worse with the automation of the instruments and procedures delivering the final results. For most operators the software is a black box. Workshops and summer (or "four seasons") schools are more essential than ever.
- Microprobe history is punctuated with a lot of unforeseen events: planned research is always an illusion.

The first commercial instrument was delivered by Cameca in 1958 (MS85), only three years after the prototype! More than ten others manufacturers built wavelength dispersive spectrometers in the sixties. Nowadays two companies still manufacture dedicated microanalysers EPMA (CAMECA and JEOL).

Today, these manufacturers supply fully automated instruments able to give us a non-destructive quantitative elemental chemical analysis of materials from beryllium upwards. The analysed volume is around one cubic micrometer in normal use. A large part of the chemical knowledge of materials at a fine scale is the result of EPMA. The actual power of computers gives us quantitative X-ray images of some square millimetres with a resolution of less than micrometer and an analytical precision better than one hundredth. Under the guidance of Raimond Castaing, Françoise Pichoir and Jean-Louis Pouchou have developed a more accurate description of the $\varphi(\rho z)$ function [7] and a new correction procedure (PAP model [8]). An improvement of this model allows the characterization of thin layers on a substrate [9].

The Secondary Ion Mass Spectroscopy

Raimond Castaing remembered with pleasure that he had started his research career by TEM observation

of thin foil of metals alloys and he never forgot the beauty of the images. So he was anxious to obtain beautiful images from samples without using the “artifice” of scanning. Castaing asked one of his students, Georges Slodzian, to study, within a short-term project, the secondary electron emission obtained by means of an ion beam impinging on a solid specimen. This work showed that the contrast obtained was related to the nature of the material. On the basis of these first results, Castaing decided in 1957 to build a secondary emission ion microscope based on the possible use of characteristic secondary ion emission as a microanalytical tool [10].

Many problems were to be solved: because of ion neutralisation by electrons, was the signal obtained characteristic of the sample? Oil vapour from the vacuum pumps was cracked under the beam and contaminated the surface of the sample. In this condition, was it possible to see a signal from the sample with a low brightness ion source? As ion images are difficult to observe and to photograph, an image transformer was needed. How was it possible to extract from one glow ionic image one type of ion?

All these problems were solved by Slodzian under the guidance of Castaing. An ion-electron converter was developed to enhance the brightness of ion images. The sputtering of the sample by the ion beam induces a cloud of ions characteristic of the local volume. In order to know the chemical composition, the mass spectrometer seemed to be the right instrument, but if filtered images of the same quality as the non filtered images are wanted, a quite specific spectrometer is needed. This spectrometer must be stigmatic, achromatic and free of distortions. The apparatus was designed, calculated, assembled and optimised, within

a few years, demonstrating the validity of the secondary-ion microanalysis as a function of depth in 1962 [11, 12].

Today’s instruments are able to perform analysis in depth with a spatial resolution of a few nanometer and a sensitivity of a few parts per billion, and surface analysis with a high sensitivity and specificity. Moreover an ion microprobe was recently developed by Slodzian combining secondary electrons and ions imaging in order to answer the permanent need for a combination of high resolution imaging and chemical analysis (Fig. 5).

The Castaing-Henry Filter

Reflecting to his success with ion images and utilising his great knowledge of TEM and of electron optics, Raimond Castaing had the brilliant idea of introducing an energy filter inside the electron microscope, an idea the realisation of which was the subject of the thesis of Lucien Henry (1964). Incidentally, let us emphasise that Castaing had a marked preference for optics-based imaging rather than scanning and image reconstruction. The filter he designed was composed of a symmetric system of a triangular magnetic sector associated with an electrostatic mirror [13]. This type of filter is still used for some applications – including the Omega filters, which are entirely magnetic – but few microscopists are using it because of practical difficulties. Electron spectrometers at the bottom of the column are now more frequent for routine work. But the main idea initiated by Castaing – i.e., the use of energy filters for better images and for local analysis thanks to electron energy losses – was the first step in the development of a powerful and popular tool, EELS.

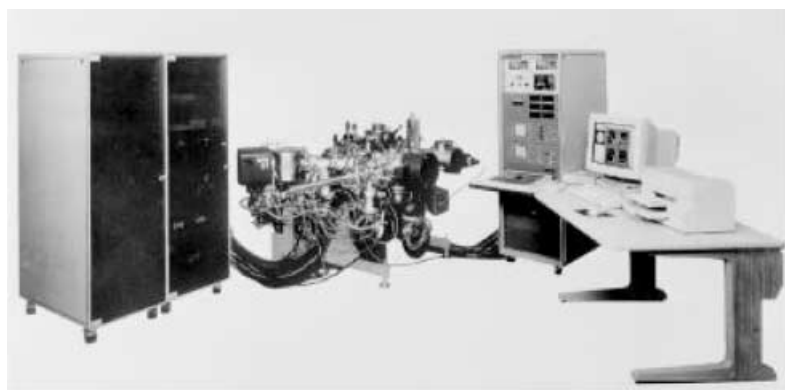


Fig. 5. The Cameca nanosims 50 ion microprobe

Others Instruments

In 1960 the analysis of light elements with the electron microprobe was not possible. At this time Castaing attempted to make by sputtering, without success, a multilayer monochromator. A new project, called “light element microprobe”, was later launched at ONERA. This project was successful [14]. The instrument used a Ross double filter for selecting X-rays and an electron column able to work at voltages between 600 V and 10 kV, gave images of light elements, which were quite new at the time. But the new instruments which appeared in the 70's stopped this development.

Many other local (point) analysis instruments have been developed since, based on the same concepts as Castaing's, such as Auger microscopes, the proton microprobe, laser excitation, the Raman microprobe, the LEXES microprobe...

Concluding Remarks

Instrumental physics creates new instruments that opens the way to new investigations on materials and to new materials and new thermal treatments. But such instruments cannot be developed just as nice toys for physicists. Their development requires close contacts with metallurgy and materials research laboratories, in order to keep aware of the real needs in these fields. A close collaboration with such research institutes as ONERA or IRSID permitted to Castaing and his students to keep these contacts active [15]. We have seen the inspiration for Castaing's microprobe was the detection of GP zones. But applications were actually not limited to metallic materials. Castaing from the very beginning contributed to studies on micrometeorites [16]. Subsequently a laboratory of the Faculty of Medicine become interested and in the late fifties Dr. P. Galle investigated applications to kidney tissues [17]. The applications of the electron microprobe and secondary ion analysis to the biomedical field are numerous.

Such close contacts are an imperative condition for the success of instruments that they will not remain just a curiosity (physics laboratories have plenty of

such nice set-ups, without any real users), but will become machines that are found in hundreds of laboratories all over the world. Historical parallels occurred with the secondary ion based instruments, with metallurgists (diffusion studies in metals and ceramics) and geophysicists (specially for the determination of isotopic ratios) finding real research benefits. But serendipity was not absent: most of SIMS instruments are now used in the semiconductor industry, an application that was not even envisaged by the inventors.

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