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A. Chamel, J.-F. Eloy. MICROANALYSIS WITH THE LASER PROBE MASS SPECTROGRAPH (LPMS) IN PLANT BIOLOGY. *Journal de Physique Colloques*, 1984, 45 (C2), pp.C2-573-C2-576. 10.1051/jphyscol:19842131 . jpa-00223801

HAL Id: jpa-00223801

<https://hal.science/jpa-00223801>

Submitted on 4 Feb 2008

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MICROANALYSIS WITH THE LASER PROBE MASS SPECTROGRAPH (LPMS) IN PLANT BIOLOGY

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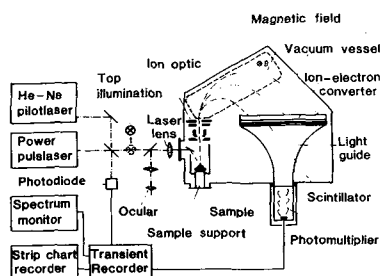
Résumé - Dans le spectrographe de masse à sonde laser un spectromètre de masse analyse les ions libérés durant le bombardement de l'échantillon par un faisceau laser. Cette technique permet l'analyse chimique élémentaire en différents points de la surface considérée jusqu'à une certaine profondeur. Cette technique a été utilisée pour les problèmes suivants : localisation d'éléments apportés par voie foliaire, composition élémentaire de tissus ou microstructures et analyse d'imprégnations du bois.

Abstract - In the laser probe mass spectrograph a mass spectrometer analyzes the ions liberated during the impinging on the sample with a laser beam. This technique allows elementary chemical analysis at different points on the considered surface down to a certain depth. This technique was used to study the localization of elements deposited on leaves, the elementary composition of tissues or microstructures and impregnations of wood.

DESCRIPTION OF THE APPARATUS (Eloy (1974), Eloy (1980))

The apparatus (fig. 1) comprises :

a) a pulsed high power laser beam (Nd/YAG laser with frequency doubler and tripler) for probing the sample surfaces ;



b) an ion source : this device works by absorption reflection mode and a plasma is emitted from the target tissue. The ions of the plasma are accelerated, then analyzed in a magnetic sector mass spectrograph ; the new version of the apparatus separates the ions in the time-of-flight mode. The detection system consists in a photographic plate (LPMS I) and, by now, in the LPMS II, in a panoramic electrooptical detector.

Fig. 1 : Laser probe mass spectrograph (LPMS).

APPLICATIONS

- Localization of elements deposited on leaves (Chamel (1978), Chamel et al (1981)) :

The LPMS was used to determine the localization of exogenous elements as a function of the depth, at the exact place of the deposit. This is important with micronutrients for a better understanding of the physiological significance of the non translocated fraction, which often represents the greatest part of the uptake. Two examples concerning copper and boron are reported fig. 2 and 3. The results show that the copper concentration decreases rapidly with depth from the treated surface. The sensitivity of the method did not permit to detect copper deeper than 20 μm and sometimes much less (thickness of the leaf blade : 0.2-0.5 mm). Inversely, results with boron show that this element does not remain concentrated just under the

surface but presents a homogeneous distribution in depth along the analyzed profile, which suggests that it penetrates deeper into the blade.

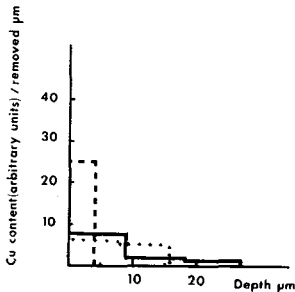


Fig. 2 : Distribution in treated part of copper deposited on a maize leaf as a function of analysis depth (5 weeks after an application of droplets of cupric acetate 0.5 mg Cu/ml).

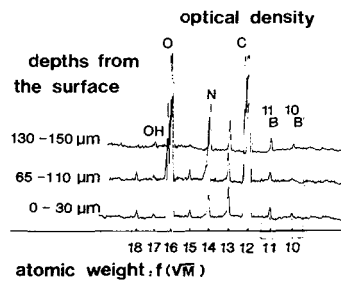


Fig. 3 : Analysis of boron at different depths from surface in treated part of a radish leaf (thickness of the leaf blade at the spot of analysis was 150 μm).

This technique was also used for analyzing zinc applied as fungicides (Table I). It is shown that zinc is detectable 24 hours after the foliar application only in a surface zone of a maximum depth of 30 μm (Chamel et al (1982)).

Table I : Analysis of Zn applied as fungicides, in the lamina of a maize leaf from the treated surface inwards (in relative atomic units).

	C a l y r a m			M Special		Polyram	Combi
	1	2	3z	1	2	1	2
0 - 30 μm	0.68	0.82	6.44	0.08	N D	1.18	0.80
30 - 60 μm	ND ^y	ND	ND	ND		ND	ND
60 - 90 μm							
90 - 120 μm							
120 - 160 μm							

z 1, 2, 3 : values corresponding to different analysis axes ;
y ND : not detectable.

The thickness of the leaf blade at the point of the analysis was 160 μm.

This method can be used when the considered element is not detectable in the non treated tissues ; in the other case it would be possible to use enriched stable isotopes.

- Determination of the elementary composition of tissues or microstructures :

= Intraroot vesicles in endomycorrhiza of *Trifolium pratense* (Strullu et al (1983))

The fungal vesicles (200 to 300 μm) were analyzed on fixed and unfixed samples. The comparison between them has shown that the fixatives and embedding procedures are not convenient for elements such as K. The diameter of the impact varied from 10 to 15 μm and the depth eroded by each laser pulse from 1 to 20 μm. The principal elements detected in vesicles are K, Ca, Mg and Na (fig. 4).

= Analysis of root nodules of *Leguminosae* :

The analysis made in the red zone at leghemoglobin of untreated nodules (about 1 by 2 mm) of *Trifolium pratense* and *Albizia lophanta* shows relatively homogeneous results for the two species. Numerous elements were detected in the nodules, C, N and O characteristic of the organic matrix were well represented. The major elements were present, particularly K, followed by Na, Ca and Mg and several others (fig. 5).

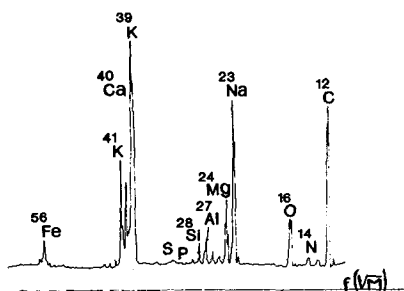


Fig. 4 : Example of mass spectrum obtained in the case of analysis of intraroot vesicles in endomycorrhiza of *Trifolium pratense*.

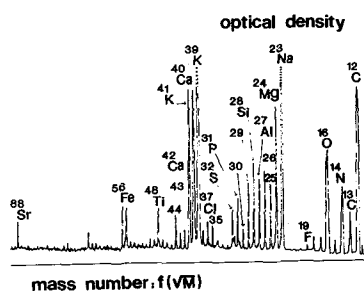


Fig. 5 : Example of mass spectrum obtained in the case of analysis of root nodules of *Leguminosae*.

LPMS is a very interesting tool for analyzing microstructures, either when the sample size is very small, as for root nodules, so that it is rather difficult to gather enough material for most of the other analytical methods, or when a specific zone inside a biological structure has to be analyzed without being isolated, as in the case of intraroot vesicles in endomycorrhizas.

= Analysis of wood impregnations :

The analysis of the wall of a wood vessel of a piece of wood impregnated with a commercial solution containing Cr, Cu, As, showed essentially a great heterogeneity in the distribution of these elements, and also a significant accumulation of Cr, Cu and As in the pitted zone of the wall (Deon (1981)).

The examples considered demonstrate clearly the possibilities of the LPMS for the analysis of bulk samples. The main characteristics of this apparatus are reported in Table 2.

Table 2 : Principal characteristics of LPMS.

	LPMS I	LPMS II
Analyzed samples	Bulk samples without special treatment	
Diameter of the analyzed zone . .	10 - 100 μm	3 - 100 μm
Spatial resolution : - lateral . .	5 - 10 μm	1 - 3 μm
- in depth	$\approx 1000 \text{ \AA}$	minimal value 200 \AA
Laser	Nd - YAG	
Wavelength	1.06 μm , 530 nm, 353 nm, 265 nm	
Pulse duration	3 - 4 ns	
Laser fluxes necessary to create a cold plasma	$10^9 - 10^{10} \text{ W/cm}^2$	
Mass spectrometry	Magnetic analyser	Combined magnetic sector and time-of-flight
Mass domain	All elements and isotopes of the periodic table	
Mass resolution	Photographic plate : $M/\Delta M = 600$ (for Pb)	Time-of-flight : $M/\Delta M = 100$ (for Ag)
Detector recorder : ratio maximum signal/minimum signal	10^3 to 10^4 with photoplate detector	5×10^2 with optical converter detector
Detection limits	$10^{-10} - 10^{-13} \text{ g}$	10^{-16} g
Detectable concentration	1 - 100 ppm	
Reproducibility	5 - 50 %	
Mass spectra	Principally monoisotopic ions	
Possibilities for quantitative analysis	Yes	

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