

Table 2.

Membrane	$t_{Li^+}$	Ref.
Poly (vinylidene fluoride-co-hexafluoropropylene)-based composite polymer electrolyte	0.3-0.5	3
Composite polymer electrolyte based on poly(ethylene oxide)-lithium tetrafluoroborate (addition of sulphatepromoted superacid zirconia)	0.42±0.05 (0.68±0.05 with S-ZrO <sub>2</sub> )	14
Lewis-acid modified polymer (LiBF <sub>4</sub> / ethylene carbonate + diethyl carbonate + triethylphosphate)	~0.6	2
Copolymer electrolyte: poly(laurylmethacrylate) and PEO-based poly[oligo(oxyethylene)methacrylate] + polyethylene glycol dimethyl ether and doped with LiCF <sub>3</sub> SO <sub>3</sub>	0.5 (room temp.)	15
Poly(acrylonitrile)-based gels (using lithium salts like LiN(CF <sub>3</sub> SO <sub>2</sub> ) <sub>2</sub> )	> 0.5 (enhanced to 0.7)	12
Poly(methyl methacrylate) as polimer matrix and different electrolytes	0.2-0.7	12, 16

### 3. The electrochemical stability window

The electrochemical stability (decomposition voltage) of the polymer electrolyte membrane can be measured by linear sweep voltammetry. The working electrode is usually a stable metal electrode (platinum, stainless steel) or acetylene black, lithium metal being the counter and reference electrode.

The potentials for anodic oxidation (anodic stability) for some membrane electrolytes, obtained by linear voltammetry, are presented in Table 3. The electrochemical stability windows are sufficiently wide for using the membranes in lithium batteries. The high values make them to resist for overcharge abuse in rechargeable Li-based batteries, which have a high working voltage by itself.

Table 3.

Membrane	Anodic limit	Ref.
Poly (vinylidene fluoride-co-hexafluoropropylene)-based composite polymer electrolyte	> 4.7 V vs Li/Li <sup>+</sup>	3
Polymers containing ethylene oxide groups linked with phosphate groups, LiClO <sub>4</sub>	6 V vs Li/Li <sup>+</sup>	4
Microporous polyethylene with highly conductive solvent-free polymer electrolyte based on poly(oligo [oxyethylene] oxyterephthaloyl)	> 4.4 V vs Li/Li <sup>+</sup>	10
Solid polymer electrolyte membranes prepared by photopolymerisation of poly(ethyleglycol)methacrylic oligomers in the presence of a lithium salt	5 V vs Li/Li <sup>+</sup>	11
Copolymerization of methylmethacrylate monomer onto polyethylene separator	4.6 V vs Li/Li <sup>+</sup>	17
Poly(lauryl methacrylate)- <i>b</i> -poly[oligo(oxyethylene) methacrylate]-based block copolymer electrolytes	~4 V vs Li/Li <sup>+</sup>	15

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## MASS-SPECTROMETRY USED IN CHARACTERIZATION OF PIGMENTS

Gheorghe Iliu, Cornelia Crasmareanu, Smaranda Iliescu, Lavinia Macarie, Nicoleta Plesu, Adriana Popa

Institute of Chemistry Timisoara of Romanian Academy, 24 Mihai Viteazul Blv., RO-300223  
– Timisoara, Roumania, email: gheilia@yahoo.com

### ABSTRACT

Naphthol AS pigments synthesised by RPTC were characterized by M<sup>2</sup> mass spectrometry. The results show that this technique is not very a reliable method for characterization of such compounds.

### INTRODUCTION

Synthetic organic pigments are carbon based molecules manufactured from petroleum compounds, acids, and other chemicals, usually under intense heat or pressure. The techniques for producing these substances on an industrial scale were invented after 1860, which created the modern era of consumer color.

Chemical and industrial innovations increased at an astonishing pace through the end of the 19th century and have continued up to the present.

Synthetic organic pigments are fabricated from a limited number of elements. The color creating aspects of the molecule depend on the chromophore, a pairing or grouping of atoms that create a complex and shifting cloud of electrons across the electron shells of two or more atoms. These electron transitions permit efficient absorption of specific light wavelengths, which creates a color that is the *visual complement* to the absorbed light (a compound absorbing in the "blue" and "violet" or short wavelengths appears to have a yellow color; a compound absorbing in the "green" wavelengths appears to have a purple color, etc.).

Other groups of atoms called auxochromes influence the pigment color by altering the light absorbing capacity of the chromophores, usually in the long wavelengths.<sup>1</sup>

Naphthol. (*Naphthol* is a registered trademark of Hoechst AG; the generic label for the same compounds manufactured by other companies is *naphthol*, with a second h. The word is from the Greek for "mineral oil", and salutes the origin of these pigments in petroleum.) Developed and patented in 1911, the naphthol compounds represent the single largest group of azo dyes and pigments. (In fact, about 20% of all synthetic organics available, over 50 in the red category alone, are naphthol pigments).<sup>2</sup>

Originally used as cotton dyes, they were soon laked as pigments and were first used in artists' paints in the 1920's. The most important group for artists is the naphthol AS pigments.

The color range is concentrated in the long wavelength end of the spectrum, including warm orange (PO24, PO38), scarlet (PO5, PR188, PR261), many reds (PR2, PR3, PR5, PR7, PR8, PR9, PR17, PR22, PR112, PR150, etc.), carmines (PR23, PR146, the many pigments listed under PR170), maroon violet (PV13, PV25, PV44), and brown (PBr1).<sup>3</sup>

In this paper we present the characterization of some Naphthol AS pigments by Mass Spectrometry

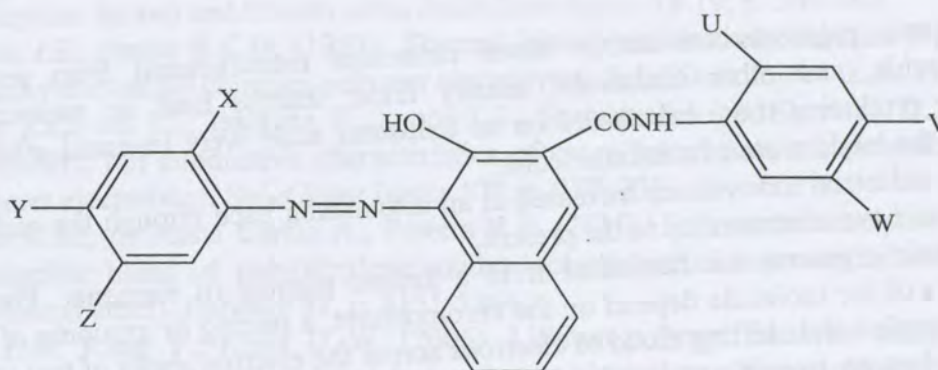
## MATERIALS and METHODS

### Spectra recording

Mass spectra were obtained using a mass spectrometer Esquire 6000 ESI (electrospray ionization) from Bruker-Daltonics. The compound was diluted before measurements at 5 pmol/ $\mu$ l in acetonitrile containing 5% ammonia and was injected in electrospray chamber by direct infusion, with a constant flow of 240  $\mu$ l/h. The mass spectra were obtained in the positive mode.

## RESULTS AND DISCUSSION

The pigments were obtained by RPTC technique when a mixture of benzenediazonium chloride in water, and 3-hydroxy-2-carboxylic acid anilides in nitrobenzene and perfluorooctyl potassium sulfonates (PFOSK<sup>+</sup>) as catalyst, was vigorously stirred at room temperature (Figure 1 and Table 1).



Scheme 1. Structure of pigment, I, II and III

Table 1. Analyzed pigments

Dye	X	Y	Z	U	V	W	Molecular formula	M
I	H	NO <sub>2</sub>	H	H	OCH <sub>3</sub>	H	C <sub>24</sub> N <sub>4</sub> O <sub>5</sub> H <sub>17</sub>	441
II	H	NO <sub>2</sub>	H	NO <sub>2</sub>	H	H	C <sub>23</sub> N <sub>5</sub> O <sub>6</sub> H <sub>14</sub>	456
III	H	NO <sub>2</sub>	H	C <sub>2</sub> H <sub>5</sub>	H	H	C <sub>25</sub> N <sub>4</sub> O <sub>4</sub> H <sub>19</sub>	439

Various analytical methods of analysis have been successfully used for the study of synthetic organic pigments, structural characterization by microscopic techniques and X-ray diffraction, and chemical analysis and colour measurement by spectroscopic methods, such as VIS spectrophotometry, IR, NMR, and MS.

The use of MS for the analysis of synthetic colorants has been surveyed by Van Bremen, with a particular emphasis on the benefits of various ionisation methods. In figures 2-4 are presented molecular peaks fragmentation of analyzed pigments.

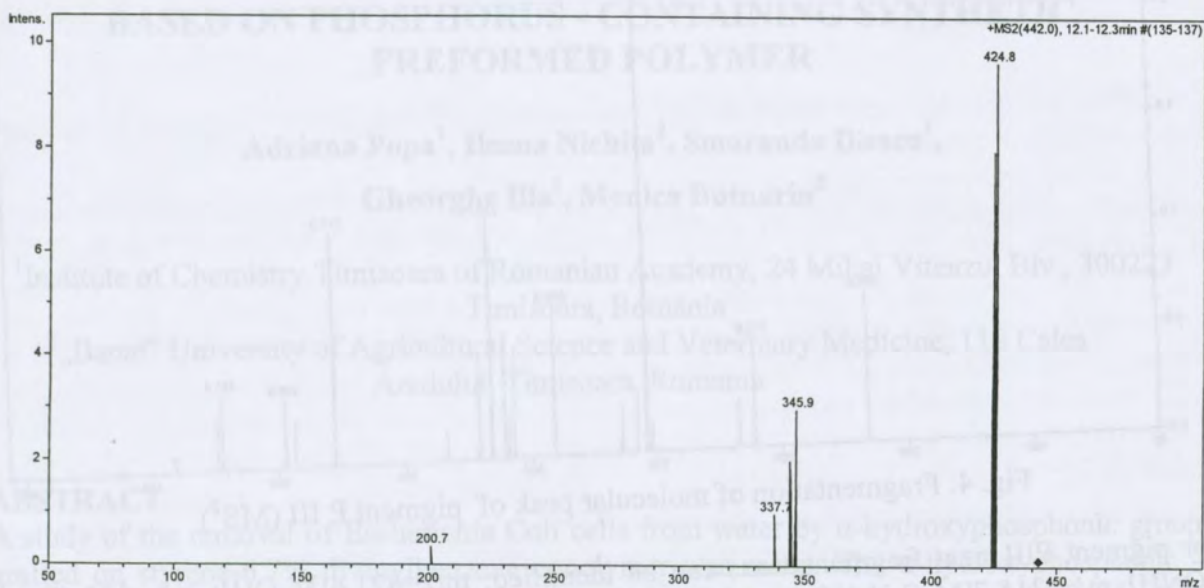


Fig. 2. Fragmentation of molecular peak of pigment P I (MS<sup>2</sup>)

Mass spectra were obtained in the positive mode. In figure 2 it is shown the positive ion mass spectrum of pigment I. By eliminating the positive ions can be identified only one peak  $m/z=426.0$  [M-O].

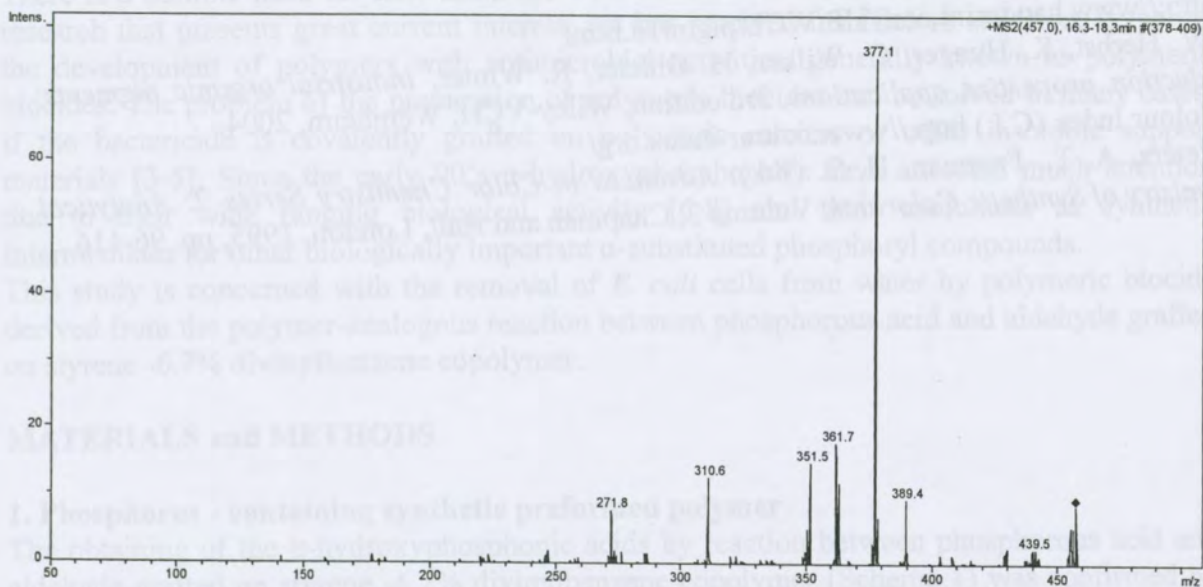


Fig. 3. Fragmentation of molecular peak of pigment P II (MS<sup>2</sup>)

In figure 3 is presented MS<sup>2</sup> spectrum of compound II. The next fragmentations could be identified as:  $m/z=439.5$  [M-O];  $m/z=410.0$  [M-NO<sub>2</sub>].

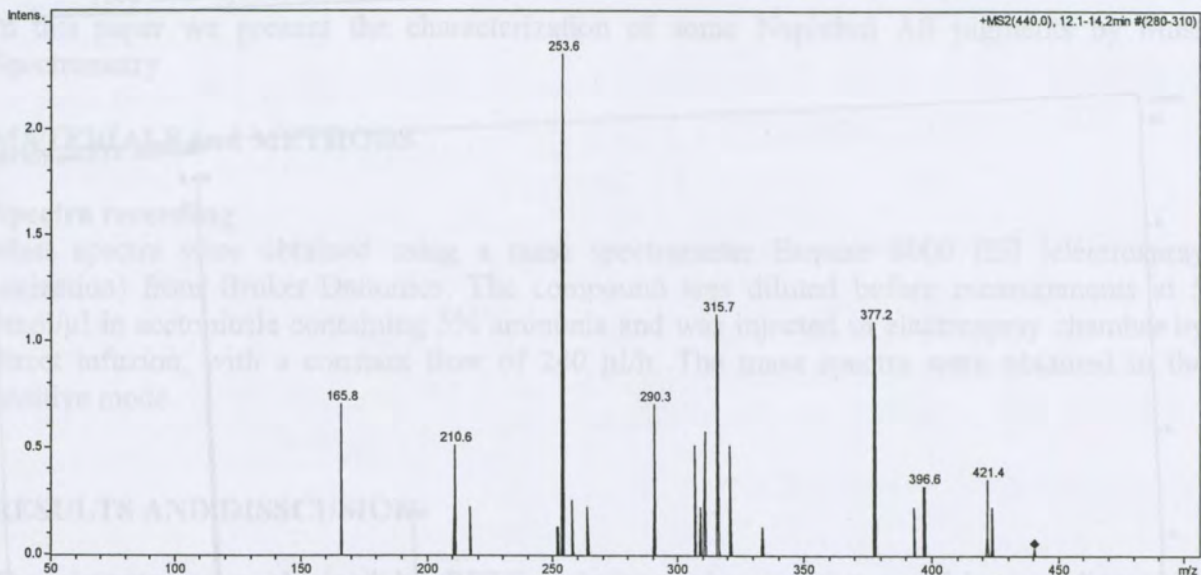


Fig. 4. Fragmentation of molecular peak of pigment P III (MS<sup>2</sup>)

For pigment PIII next fragmentations can be identified: m/z=421.4[M-OH]; m/z=396.6[M-CONH], m/z=315.7[M-C<sub>6</sub>H<sub>4</sub>NO<sub>2</sub>]; m/z=290.3[M-N=N-C<sub>6</sub>H<sub>4</sub>NO<sub>2</sub>]

### CONCLUSION

Mass spectrometry applied to characterization of Naphtol AS pigments is not a very reliable method when positive mode is used for MS<sub>2</sub> spectra

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