

# **LIBS: an innovative technique to improve the knowledge of bitumen elemental composition : meeting the challenge of metal analysis in an organic matrix**

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## **ABSTRACT**

*Main bitumen properties are obtained by standard tests. Analytical techniques can be used to ascertain their chemical structure but not fully, due to the complexity of bitumens. For several years, variability in the quality of bitumen has been observed. The conventional laboratory tests performed on bituminous materials are unable to identify any difference between the binders in question. An innovative technique rapidly establishes itself to determine the elemental composition of materials. This method, known as Laser Induced Breakdown Spectroscopy (LIBS), uses a laser coupled with an optical emission spectrometer. We have adapted the LIBS protocol to make it suitable for the characterization of bituminous materials. This method is compatible with the precepts of sustainable development because, amongst other things, it does not use any solvents and generates no waste. This paper explains the principle of the LIBS technique, the necessary equipment, the way it is set up and practical applications in the field of road construction.*

**Keywords:** Chemical properties, Safety, Testing

## 1 Introduction

In today's context of global warming, it is necessary to find ways of limiting the environmental impact of every technical field and encourage more environmentally responsible approaches. The pervasive presence of roads requires the sector to set an example. The highways industry has been committed to this type of policy for many years, for example by recycling material from old pavements. This has allowed us to considerably lower consumption of new pavement materials, conserve natural resources and reduce stockpiles of waste materials. The industry is going even further in this direction by making use of methods that are more environmentally friendly, particularly in the case of the analysis techniques for characterizing the materials it uses. Bitumen, which is of fundamental importance for roads, is subjected to particularly detailed analyses because in recent years it has been observed to exhibit a degree of variability due to the difficulty of obtaining crude of sufficient quality.

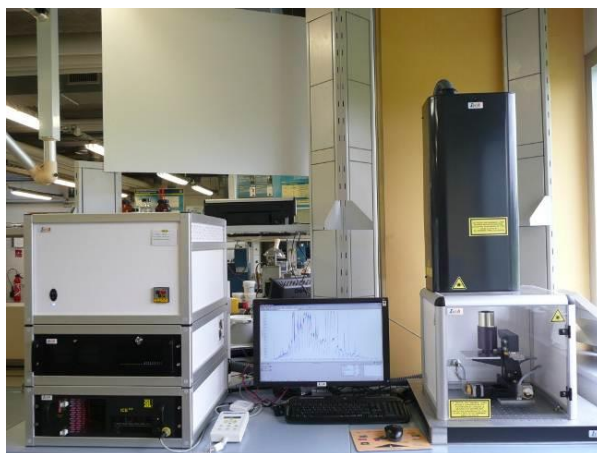
For roads to be durable, the materials used in them must have long-lasting properties. It is therefore necessary to check the quality of bitumens. Conventional bitumen characterisation techniques provide an initial picture of their properties, but give us no certainty as to their intrinsic quality. The reason for this is that the intrinsic quality does not depend on the empirical characteristics of the bitumen, but on its chemical composition. However, the latter is complex as bitumen is made up of thousands of different highly complex molecules. The use of new analysis methods is therefore essential to improve our knowledge about the material.

The current issues we are experiencing with bitumens are due to the variability in their quality, the possible presence of contaminants and the origin of the crudes. In this connection, it has been found that the presence and concentration of certain metals affects the potential uses of bitumens (bitumen in emulsions for example).

A range of techniques are available for determining the metal content, for example flame absorption spectroscopy and the plasma torch. These techniques are relatively complex to perform in the laboratory and are generally only used with appropriate justification (for example, in the case of an expert appraisal) and on a limited number of specimens. They are not appropriate for the systematic analysis of bitumens which limits the possibilities of creating a database, carrying out follow-up studies and taking preventive measures.

In recent years (Green News Techno 2009), (Romero et al. 2010), (Haider et al. 2013) LIBS (Laser Induced Breakdown Spectroscopy) technology has come to be seen as an alternative to the analysis methods mentioned above. LIBS provides a way of analysing the elemental constituents of a material. It is compatible with our company's policy of environmentally responsible development as it is straightforward to perform, rapid (it only takes about ten minutes), contact-free, minimally destructive, and produces no effluent emissions. The results are obtained immediately, and as the technique does not require samples to be taken, management and traceability are much less problematic. The implementation costs are therefore very low. This technique is rapidly establishing itself and a range of equipment is currently available on the market.

We have therefore adapted the analysis protocol to the appraisal of bitumens thus developing an innovative analysis technique for their characterisation (Figure 1). Its advantages compared to conventional techniques and its potential applications are outlined below.



**Figure 1: LIBS: an innovative device for analysing bitumen**

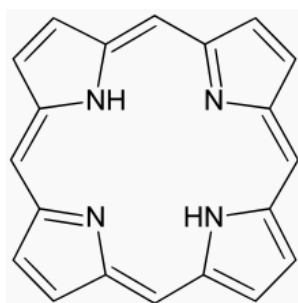
## 2 Metallic species in bitumens

### 2.1. Chemical structure

Bitumen is mostly composed of hydrocarbon molecules, with some heterocyclic species and functional groups containing sulfur, nitrogen and oxygen atoms. Bitumen can also contain trace amounts of more than 20 different metals such as nickel, vanadium, iron, calcium and magnesium. Those metallic elements, mentioned later in the publication (figure 5), are compatible with bitumen organic matrix, in the specific form of organic – inorganic complexes. They can occur in the form of metallic salts (derivate from organic molecules such as carboxylic acids), oxides, or porphyrin-type complexes.

Porphyrins are complex organic compounds that occur naturally. Hemoglobin and chlorophyll are examples of porphyrins associated with metal atoms.

Figure 2 shows the base structure of a porphyrin. Porphyrin contains four nitrogen atoms, which can be bond with a metal atom to result in a metalloporphyrin. It is a highly stable, fully aromatic structure.

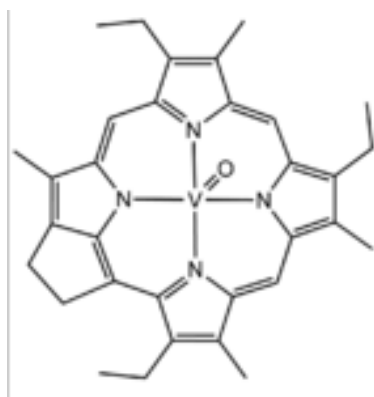


**Figure 2 :porphyrin core structure**

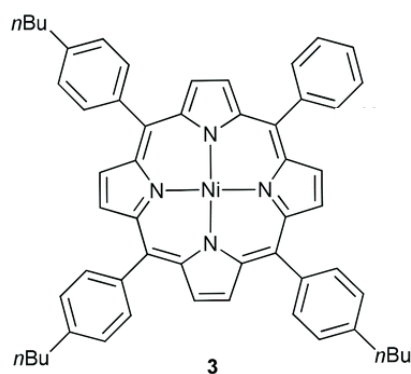
It has been known since the 1930s that bitumens contain metalloporphyrins, from analytical work that identified iron and vanadium and, consequently, established the link between marine plant chlorophyll and petroleum genesis.

A porphyrinic core can be included in a larger structure, with various ring substituents, leading to a quasi-infinite variety of molecules.

Some examples are shown in the figures 3 and 4.



**Figure 3**  
**Vanadium porphyrin extracted from crude oil**



**Figure 4**  
**Model Nickel porphyrin in bitumen asphaltenes**

The formation of organic – inorganic complex structures is the main reason why metallic elements can be stable in a bitumen organic matrix. Therefore, the detection and quantification of metallic compounds requires the use of a method whose result does not depend on the organic fraction itself. Even sodium, which can be found in crude oil in the form of sodium chloride, has to be separated from organic matrix for analysis.

Two main principles can be followed :

- The use of a spectroscopic method towards which organic phase appears transparent, described later in the text (atomic absorption spectroscopy)
- The elimination (burning) of the organic phase in which metals are clustered, along with metal analysis (2 methods described later in the text : ICP and LIBS).

## 2 General description

### 2.1 Comparison between LIBS and other techniques for the determination of metal contents

Three techniques (Diaz Rosadoa 2013) can be used to determine the Na, Ca, Mg, V and Ni contents of bitumen:

- Plasma torch (ICP-AES or ICP-OES) or Inductively Coupled Plasma Atomic Emission Spectroscopy or Inductively Coupled Plasma Optical Emission Spectroscopy
- Atomic Absorption Spectroscopy (AAS)
- Laser Induced Breakdown Spectroscopy (*LIBS*)

Inductively coupled plasma atomic emission spectroscopy (ICP-AES) consists in injecting the sample into a plasma produced from argon or helium (a plasma is a gaseous mixture from ions, electrons and atoms) and sustained with an external radiofrequency (RF) electric current. This inductively coupled plasma produces excited atoms and ions that emit electromagnetic radiation at wavelengths characteristic of a particular element, while they drop from the excited state back to the ground state. The intensity of this emission is indicative of the concentration of the element within the sample.

Atomic absorption spectroscopy method relies on the principle that free, uncombined atoms will absorb light at specific wavelengths corresponding to the energy requirements of the specific atom.

Atoms in the ground state absorb light and are excited into a higher energy state. Each transition between energy states is characterized by a different energy, and therefore a different wavelength of light. The amount of light absorbed is proportional to the concentration of the atoms over a given absorption path length and wavelength. Standards of known concentration are prepared, matched to the sample matrix, and measured.

Those first two techniques, which have been in common use for several years, have many drawbacks. At the outset, it is necessary to prepare specimens, which requires the use of relatively dangerous solvents such as nitric acid during mineralisation in the case of ICP or nitric acid and xylene in the case of AAS.

In addition, Atomic Absorption Spectroscopy uses gases such as acetylene (which is inflammable and burns in the presence of air or any other oxidising agent, and which may also create explosive environments), or nitrous oxide (NO<sub>2</sub>) whose major danger is asphyxiation due to a lack of oxygen. In addition, it is classified as a pollutant in the Kyoto protocol as it is a greenhouse gas and the fourth most important contributor to global warming after water vapour (H<sub>2</sub>O), carbon dioxide (CO<sub>2</sub>) and methane (CH<sub>4</sub>). Its global warming capacity is 310 times that of CO<sub>2</sub>. ICP, on its side, requires the use of considerable quantities of argon.

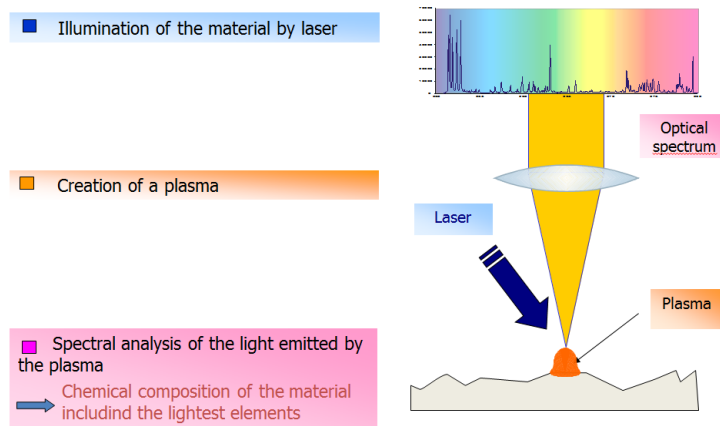
These analytical techniques are relatively complex and also have other disadvantages. Sampling creates a degree of uncertainty, the preparation and analysis processes are relatively long (between three hours and one day), and these techniques are destructive and therefore consume materials.

As it is so simple to perform, LIBS can be used to analyse the elements in a material without the need to prepare specimens, or use solvents or gases and only affects a very small piece of material that is a few tens of micrometres long and a few micrometres deep. Its advantages can be summed up in two words: speed and simplicity.

### 2.2 The principle of LIBS (Laser Induced Breakdown Spectroscopy)

LIBS has existed for some time, the technique was developed 1963. It is based on the information that is emitted during the interaction between a laser beam and the material, a phenomenon observed by Maiman in 1960 shortly after the invention of the laser. The general principle is very simple and can be described in three stages (Figure 5):

- illumination of the material by laser,
- creation of a plasma,
- spectral analysis of the light emitted by the plasma.

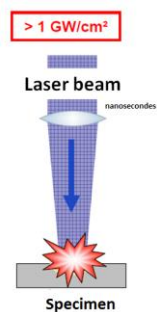


**Figure 5: The general principle of LIBS**

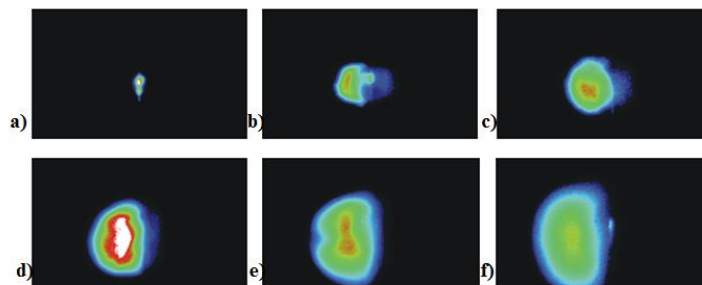
Nevertheless, the use of LIBS technology involves a considerable number of complex physical phenomena (Ismaël et al. 2009), which explains why devices for applying the technique has taken so long to appear on the market. It is necessary to concentrate the energy from a laser onto the material to be analysed in order to achieve a surface power density of the order of one  $\text{GW}/\text{cm}^2$ . This is done by focusing ultrafast laser pulses with a duration of a few nanoseconds (ns).

These conditions of intense radiation result in the immediate vaporisation of a few micrograms of material at the focal point, with the breakdown of the molecules and the creation of a plasma (Figure 6). This transfer is the result of ionisation of the vapour due to electron acceleration, and the outcome is a system consisting of atoms, ions and electrons whose composition is representative of the target under investigation.

The plasma cools as it expands into the surrounding gas (Figure 7) emitting radiation which is characteristic of the atoms and ions in the plasma. Part of this light energy is analysed by a spectrometer.



**Figure 6: Creation of plasma**



**Figure 7: Expansion of plasma**

LIBS is able to:

- carry out qualitative analysis based on the wavelengths of the characteristic emission peaks of the constituents of the specimen (ADAM and LEONE 2012),
- carry out quantitative analysis by measuring the intensity of the emission peaks, which is proportional to the number of atoms present in the measured volume of plasma (INERIS 2011).

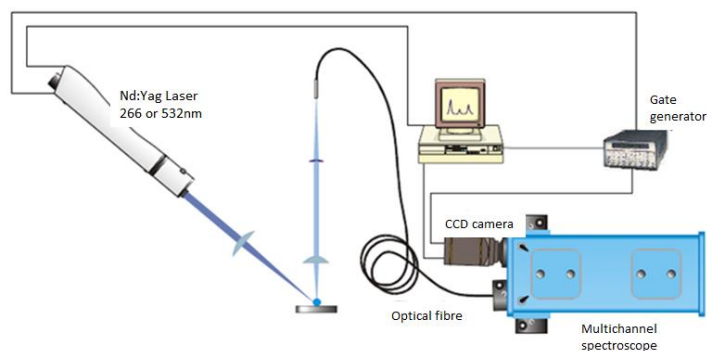
It is therefore possible to conduct an exhaustive determination of the elements present in the material, from light to heavy, as they are found in the periodic table. The periodic table shown hereafter (figure 8) shows metallic and metalloid elements which may be found in bitumens.

1																	18															
H																	He															
3	4											13	14	15	16	17	18															
Li	Be											B	C	N	O	F	Ne															
11	12											13	14	15	16	17	18															
Na	Mg											Al	Si	P	S	Cl	Ar															
19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36															
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr															
37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54															
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe															
55	56	57-71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86															
Cs	Ba											Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn						
87	88	89-103	104	105	106	107	108	109	110	111	112	113	114	115	116	117	118															
Fr	Ra											Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Uut	Ff	Uup	Lv	Uus	Uuo						
																		57	58	59	60	61	62	63	64	65	66	67	68	69	70	71
																		La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
																		89	90	91	92	93	94	95	96	97	98	99	100	101	102	103
																		Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

**Figure 8 : Mendeleev periodic table –  
Metallic and metalloid elements potentially found in bitumens in red circles.**

### 2.3 Instrumentation

The apparatus used to perform LIBS is able to analyse the elements present in all forms of material, solids, liquids or gases, quickly and without contact (Formation IVEA, 2009). A typical system is shown in Figure 9. It consists of a pulsed laser, a system for focusing the beam on the specimen, a system to collect the light emitted by the plasma and a fibre optic cable to carry it to a spectrometer that is linked to a computer that controls the apparatus, acquires the data and processes the spectra.



**Figure 9: Instruments used in a LIBS system**

## 3 LIBS and bitumen

LIBS is used on bitumens in order, amongst other things, to determine their heavy metal content using calibration line techniques.

### 3.1 Adapting LIBS for use on bitumen

The analysis of a specimen is subject to many types of bias, particularly when it interacts with its environment (the surrounding air, the supporting matrix,...). The calibration process therefore varies according to the materials and their state, which is why the standard addition method is used. Thus, bitumen specimens were prepared from bitumen and single-element standards in a non-volatile bitumen-compatible oil (Conostan® oil analysis standards also used in ICP or AA).

### 3.1.1 Calibration lines

Initially, we used the bitumen standards to optimise the parameters of the apparatus, in particular the spectrometer, so as to obtain the highest signal-to-noise ratio. This stage was necessary to eliminate phenomena such as the generation of ghost peaks and self-absorption (due to signal saturation). The goal was to define analysis parameters that could be applied to all the elements while at the same time achieving the highest possible sensitivity (which corresponds to the gradient of the calibration line: the steeper the gradient, the higher the sensitivity). We thus plotted the calibration lines which are shown in Figure 10. They allow us to determine the amount of metal in the analysed bitumen rapidly and with a high degree of precision. The high sensitivities for Na, Ca and Mg are striking, but the sensitivity is lower for V and even more so for Ni, suggesting limits with regard to the quantification of the latter.

Once calibration lines are obtained, they can be used for any bitumen, as the signal intensity does not depend on the organic phase itself. And as it is highly stable in time, it is not necessary to build the calibration line before every test series : the same chart can be used over a long time, checking only once in a while (e.g. once every month) the signal intensity on a few standards.

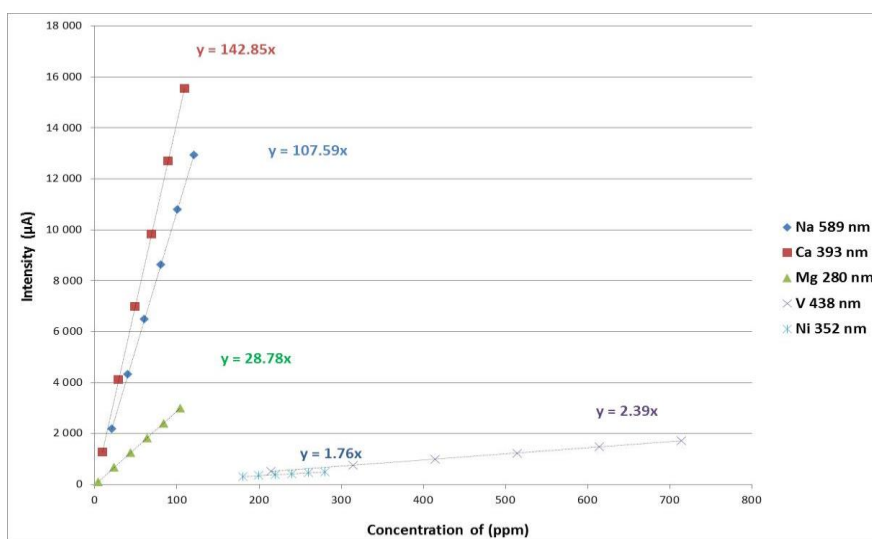


Figure 10: Calibration lines for the various elements

### 3.1.2 Precision, lower limit of detection (LLD) and repeatability

In order to conduct analyses with a high level of precision (i.e. with accurate and consistent measurements), it is necessary to make a large number of measurements to reduce the relative uncertainty. In our case, we made 25 measurements for each bitumen standard or specimen, and for each measurement, 200 shots are done.

Moreover, the lower limit of the detection (LLD, which is the minimum value of the measured quantity that can be detected) and the repeatability must both be known when analysing the results. The reason for this is that a result may not be reliable when the signal is only slightly above the background noise. The same applies for the repeatability of the analysis technique. Table 1 sets out these data for each of the control peaks for the analysed elements.

The LLDs we obtained were very low, and repeatability was satisfactory for the measurement ranges used for bitumen. However, these tests have shown that it is not possible to analyse Ni with this apparatus and these parameters as both the sensitivity and the LLD are low (below the usual concentration range of Ni).

Table 1 Lower limit of detection for the different elements and repeatability

	$\lambda$ (nm)	LDD (ppm)	Usual concentration in bitumen (ppm)	Repeatability (%)
Na	589.02	~ 1.5	10 - 100	±10
Ca	396.86	~ 0.7	0 - 20	±10
Mg	279.56	~ 1.0	0 - 20	±10
V	437.95	~ 44	200 - 800	±10
Ni	341.49	~ 72	10 - 70	Not determined

### 3.1.3 The particular case of Ni

It is difficult to determine Ni concentrations because its emission peaks have the same wavelength as those of some molecules present in bitumen. It is therefore very difficult to identify the presence of low concentrations. So, in spite of the use of specific parameters, the LLD with a multichannel spectrometer is less satisfactory than for the other elements. A different detection system with a monochromator coupled with a photomultiplier was therefore tested and gives the calibration line shown below (Figure 11) once the parameters had been adjusted.

This gave us an LLD of 3.4 ppm, which was approximately 20 times lower than with the multichannel spectrometer (Note technique IVEA 2012).

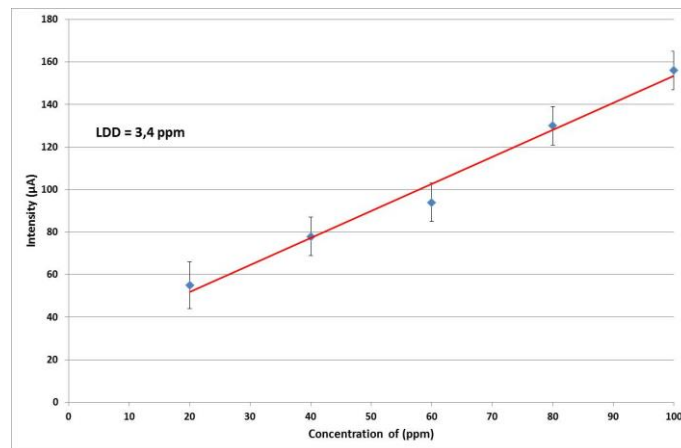


Figure 11: Calibration line for Ni with the monochromator

The usefulness of the monochromator-photomultiplier system for the quantitative analysis of Ni has therefore been clearly demonstrated. This apparatus can also be used to analyse other elements which are difficult to determine with a multichannel spectrometer.

## 3.2 Studies on bitumen

### 3.2.1 An “identity card” for bitumens

Due to our systematic analysis of the different bitumens we have built up a database and created “identity cards” for our bitumens. Figure 12 shows the metal contents for certain bitumens based on their origin. These parameters allow us to distinguish between certain bitumens in a clear and statistically significant manner, as well as to establish with certainty when there is any variation in the metal content of our bitumens.

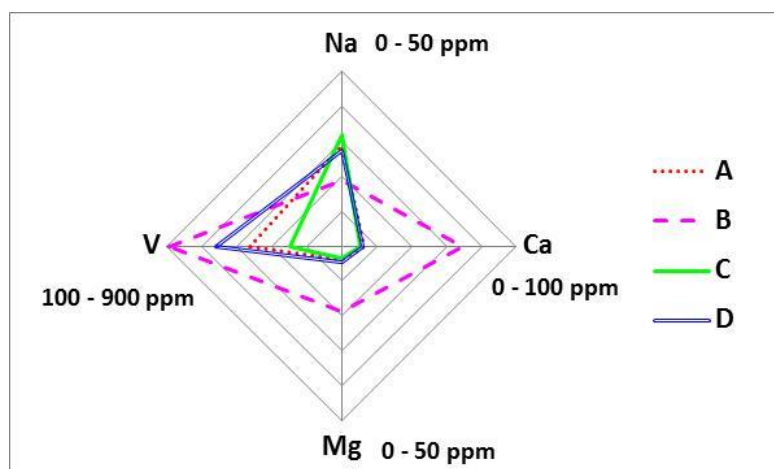


Figure 12: Identity card for different bitumens



All the bitumens present the same physical and rheological properties (35/50 penetration grade) ; the main difference comes from their origin : naphthenic bitumen for B and various paraffinic bitumens for A, C and D.

### 3.2.2 Assessment of bitumen

Below, we shall describe a LIBS analysis of a bitumen which was suspected of having caused problems on site and a commonly-used bitumen which will serve as a control.

The problem is as follows: difficulties appeared during emulsification tests on the suspect bitumen. While both bitumens produced mixes with satisfactory performance, their behaviour with regard to emulsification was markedly different: only the commonly-used bitumen could be used to manufacture emulsions with certainty, as the emulsion obtained with the suspect bitumen was so viscous that its characterisation was not possible.

In this kind of situation, the assessment is all the more important, that the use of an unexpectedly viscous emulsion can lead to difficulties during emulsion handling and application. The figure 13 hereafter shows an example of trouble encountered when laying a surface dressing. The use of a highly viscous emulsion leads to an uneven emulsion film, which may later result in a phenomenon of striping (progressive loss of chippings leaving bare areas in lines) as shown on figure 14.



**Figure 13 : uneven emulsion film during surface dressing application due to excessive viscosity of emulsion**



**Figure 14 : surface dressing striping within months after jobsite**

As a first step of assessment, the normal tests were performed and confirmed that both bitumens complied with the specifications laid down in the standard EN 12591.

The LIBS analysis (Figure 15) showed that there were differences in the metallic salt contents of the two bitumens. More specifically, the two bitumens differed with regard to their Na and Ca contents (Table 2). Both these elements are recognised as causing problems when bitumens are used in certain applications. The metal contents identified in the suspect bitumen could on their own be sufficient to explain the observed emulsionability issues.

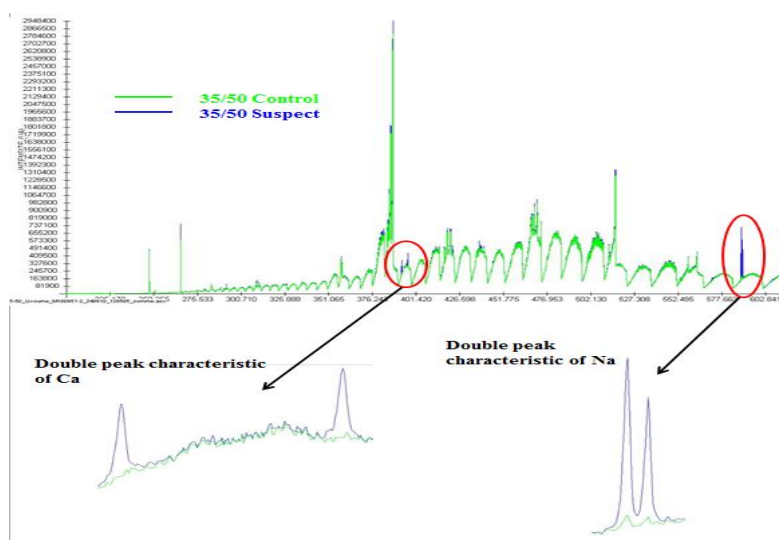


Figure 15: Spectra of the 2 bitumens

Table 2 Metal contents

Elements analysed (λ in nm)	35/50 Control Content in ppm	35/50 Suspect Content in ppm
Na (589nm)	26	~ 300*
Ca (393 nm)	2	15

\*The Na content is so high that this result is outside the calibration lines (maximum 100 ppm)

Other applications have enabled us to resolve other problems, both in the framework of expert appraisals and in a research and development setting.

#### 4 Conclusions and outlook

LIBS is the combination of a laser ablation technique with optical emission spectroscopy. It is contact-free and can be used for the exhaustive determination of the elemental composition of a material, from light to heavy elements. It is precise, rapid (taking approximately 10 minutes) and minimally destructive. It is compatible with our company’s policy of environmentally responsible development due to the fact that, as it does not use any solvents, it is more environmentally-friendly than the usual techniques for determining metal contents (ICP and AAE). Its innovative nature means this technology is still in the process of development, and its finalisation will depend on the ability to control all the parameters that are at play.

The calibration method has been validated and the first results show the technique’s ability to analyse specimens with a high degree of precision, in terms of repeatability, lower limit of detectability and sensitivity. Some shortcomings of the apparatus, which were identified during experiments, have been resolved following the acquisition of a monochromator. The availability of this analysis technique means that we are systematically able to monitor the metal content of the bitumens of different origins, which means we are able to:

- monitor how they change over time,
- recommend, or on the contrary, advise against the use of some bitumens for some applications in order to ensure that our products are of the highest possible quality.

Moreover, when we conduct expert appraisals, this technique is both less time-consuming and more effective than those used previously. This has an impact on the progress of the construction project in question and the implementation of

any remedial measures. It also allows us to maintain the quality of the products we offer our clients, in spite of the marked variability that bitumens sometimes display.

Apart from the analysis of bitumens, there are many other potential applications, for example the detection of heavy metals in contaminated soils, or aggregate testing.

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Aggregation of asphaltene model compounds using a porphyrin tethered to a carboxylic acid†

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