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Nahar, Sayeda; Schmets, Alexander; Scarpas, Athanasios

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Probing Trace-elements in Bitumen by Neutron Activation Analysis

S.N. Nahar
Section of Pavement Engineering
Faculty of Civil Engineering & Geosciences, Delft University of Technology
Stevinweg 1, 2628 CN, Delft, The Netherlands.
Tel: +31(0)152789597, Fax: +31(0)152785767, E-Mail: s.n.nahar @tudelft.nl

A.J.M. Schmets and A. Scarpas
Section of Pavement Engineering
Faculty of Civil Engineering & Geosciences, Delft University of Technology

Abstract
Trace elements and their concentrations play an important role in both chemical and physical properties of bitumen. Instrumental Neutron Activation Analysis (INAA) has been applied to determine the concentration of trace elements in bitumen. This method requires irradiation of the material with neutrons that transform the elements into radioactive isotopes. By analyzing the activity of the individual nuclides, the concentration of each detectable trace element can be determined with high precision. In this work, we perform trace elemental analyses of 13 distinct bitumens, including 2 modified and 3 bitumens from the material library of Strategic Highway Research Program (SHRP. Three elements, vanadium, nickel and cobalt are found to be present in all bitumens. Vanadium and nickel are found to be the most abundant among all the elements detected. Next to vanadium and nickel, significant concentrations of iron are found in 11 bitumens. The total number of trace elements identified varied from 17 to 28 for the bitumens studied. For modified bitumens, the concentration of trace elements is used as a parameter to measure the extent of modification. The sum of most abundant trace elements (vanadium and nickel) correlates well with the sulphur and asphaltene contents of the same bitumen. Moreover, the concentration of the latter metals are known to be an indicator for the aging characteristics of bitumen. Thus, INAA provides the content of trace elements in bitumen, where the concentrations vary (ppm to ppb) depending on the crude origin of the material. Thus, INAA can be used to trace back the crude origin of the material, which may have applications in the field of asphalt recycling (RAP and RAS).

Keywords
Bitumen, trace elements, Instrumental Neutron Activation Analysis (INAA)

1. Introduction

Trace metals are intrinsic components of bitumen and are mainly associated with the asphaltene fraction of the material (*1*). Asphaltenes are macromolecules, that are more polar in nature compared to other components in bitumen. Its chemical structure may vary within the material and depends on the type and number of structural unit (i.e. building block) that makes up this molecule. Common building blocks of asphaltene are sheets of polyaromatic rings, of which many contain small amount of heteroatoms (sulphur, nitrogen and oxygen) and trace quantities of metals (*2-4*). In the presence of trace metals, these units may form organometallic complexes that are known to influence the size of the asphaltene molecule and later also its association to larger structures. Because of the biological origin of bitumen, also natural metal-organic molecules, like porphyrins, are present. Asphaltenes are known to be the viscosity building component in bitumen, which partly originates from the affinity of these molecules to form associations. The presence of various metals can facilitate the clustering and association of the asphaltene particles (clusters with a diameter in the order of 10 to 30 nm) (*1; 5-9*).

This can be understood as follows: trace-elements, especially metals, as part of an organic molecule, leads to molecules with a high polarity. It requires only low concentrations of highly polar molecules, and the presence of polarizable molecules, to observe an effect on the material's physico-mechanical properties. One can see this as a kind of chain reaction; just a few initiators (highly polar molecules, here associated with the presence of certain trace metals) induce dipole moments in polarizable 'neighbor' molecules, and so forth. These polar molecules and induced polar molecules will form stronger associations than non-polar molecules would form. Hence physical properties like viscosity or the average size of molecular associations will be effected significantly.The size and dispersity of these clusters effect other solubility classes of bitumen in terms of mobility, hence the rheological property of the material. Thus trace metals play a significant role in the flow, and other chemomechanical, properties of bitumen (*1; 4*).

Vanadium and nickel are the most abundant trace metals, found in almost all bitumens and occur primarily in porphyrin-like organometallic complexes (*1; 5; 6*). Next to vanadium and nickel, iron is also present at significant concentration in many bitumens. Other metals such as magnesium, calcium, chromium, cobalt, zinc and molybdenum are often present in smaller quantities (*10; 11*). There are also some elements found in very small concentrations in bitumen, but their presence may very well influence the molecular interactions within the material. The concentration of these elements and relative abandance varies, depending on the source of the bitumen, thus the elemental makeup of bitumen allows to trace back to the source of the crude oil. Mixtures of bitumen from different crude sources can be unraveled in this way. This may help to trace back the original bitumen present in RAP or RAS, and will help to identify compatible rejuvenation agents for re- or upcycling these 'waste materials'.

Some researchers have tried to correlate the trace metal content to aging characteristics of bitumen. Van Gooswilligen et al. suggested that bitumen oxidation may partially be catalyzed by the organometallic complexes found in most bitumen (*12*). According to Traxler and Shelby, nickel and vanadium correlate well with the bitumen hardening index. Other researchers reported that vanadium plays a significant role in the hardening by UV radiation (*13*). Green et al. also reported on the relation of vanadium to aging and confirmed a significant influence of this metal on bitumen aging characteristics (*14*), while others found that the vanadium concentration is an indicator of propensity to oxidative aging of bitumen (*15*). Elsewhere it has been reported that nickel has the most pronounced effect on the rate of oxidation (*16*). Altogether, once the effect of trace metal concentration on the oxidation pathway of broader ranges of bitumen grades (of different origins) has been established, the trace-metal content could become a reliable and rapid predictor of the material's susceptibility to aging.

There are a few analytical techniques that are used to characterize trace elements in petroleum. These methods are: optical emission spectroscopy, atomic absorption spectroscopy, polarography and colorimetric analysis (*17*). In common practice, only the concentrations of the most abundant trace elements (vanadium, nickel and iron) are usually measured in bitumen. In the Strategic Highway Research Program (SHRP), the most abundant trace metals were measured together with the concentrations of major hetero elements (S, N and O). Inductively coupled plasma spectroscopy (ICP) was used to measure the concentrations of vanadium, nickel and iron for the eight core SHRP bitumens (*18*). ICP and the earlier mentioned techniques involve chemical separations and pre-concentration of samples, which may introduce sources of contamination and loss of volatiles (*17*). And are often not sensitive to the elements present at very low concentrations in the sample. Standards on these methods to perform these analyses on bitumen have not yet been established and the reproducibility of the results are often poor (*19*).

Here, we reintroduce a method to detect trace elemental concentrations: instrumental neutron activation analysis (INAA), a technique often used by petroleum geochemists. The technique provides a bulk analysis of the material and can measure very low concentrations of elements with high precision. One can obtain a complete trace elemental mapping by using this method. Besides, the sample preparation procedure is very simple and doesn't require any separation or decomposition of organic components. The possible sources of contamination are minimal and the elemental concentrations can be measured with high accuracy (*10; 17*).

The objectives of this study are to obtain the complete trace elemental maps and concentrations for 13 bitumens by using INAA. The materials are obtained from different sources, and include two modified bitumens and three SHRP bitumens. The concentrations of the six most abundant trace metals, i.e. vanadium, nickel, iron, chromium, cobalt and zinc, present in these bitumens, are compared. Then the concentrations of vanadium, nickel and iron of three SHRP bitumens obtained by INAA are compared to the same measured by ICP in the SHRP program. Further, a correlation is found between the total trace metal content of bitumen to fractions of hetero atoms (especially sulphur) and asphaltenes. Lastly, the consistency of elemental concentration is checked for a pure bitumen and two modified bitumens derived from it.

2. Materials and methods

2.1 Materials

The bituminous materials selected for INAA analysis are listed in Table 1. Among them, 11 are pure bitumens from different sources and the other two are prepared by modifying a selected original bitumen with two additives. AAA-1, AAM-1 and AAD-1 are selected from the bitumen library of Strategic Highway Research Program. Another four bitumens designated as D-0114, D-0113, D-0184 and B (20/30) are obtained from NYNAS, Sweden. The crude origin of bitumens BNDM 90/130 and BNDM 80/120 is Kazakhstan. Fina 70/100 has been obtained from Total and the modified bitumens (10 % w/w) are derived from this bitumen. One of the additives to the modified bitumen is ethylene vinyl acetate (EVA) and the other is Sasobit (trade name). EVA is the copolymer of ethylene and vinyl acetate and Sasobit is a synthetic wax manufactured from natural gas or coal gasification by the Fischer-Tropsch process (*20*).

2.2 Instrumental Neutron Activation Analysis (INAA)

INAA is an analytical technique for the precise determination and quantification of chemical elements at very high sensitivity (<ppb). This method is capable of analyzing various elements simultaneously and also sensitive enough to detect trace elements at very low concentrations. INAA is a technique of choice to probe the presence of trace elements in bitumen as its major constituents, carbon, hydrogen and electronegative heteroatoms (N, O) seldom form any radioactive isotope (*21*). This makes the method an effective tool to measure the trace elements within bitumen, without any interference.

The key prerequisites to analyze any sample by INAA include a source of neutrons, suitable instrumentation for the detection, analysis of emitted gamma radiation and a detailed knowledge of the radioactive activation of the elements by neutron irradiation and its characteristic gamma-ray decay emission spectrum. Figure 1 schematically presents the steps associated with an INAA experiment and illustrates the process of activation of atomic nuclei present in the bitumen by the neutron capture. In this method, the sample is exposed to a neutron flux in a nuclear reactor or any other neutron source. During the irradiation process, radioactive nuclides are produced and emit distinctive gamma rays that are detected by gamma-ray spectrometers. The wavelength or energy of this gamma radiation characterizes certain radionuclides and the intensity of the radiation is used to determine the concentration of the activated element. A specific peak in the gamma-ray spectrum corresponds to a certain element and in this way qualitatively the presence of an element is known. Further, quantitative information on the concentration of an element is obtained from the peak area.

The nuclides formed after neutron activation will have different half-lives and can be classified in three groups: (i) short (half- life seconds to hours), (ii) medium (hours to days) and (iii) long-lived nuclides (days to weeks/months) (*22*). For all the elements measured in bitumen, nuclides with short half-lives were measured in the first hours after irradiation. The medium-lived radionuclides were measured between 3 to 6 days and the long lived nuclides were measured 3 weeks after irradiation.

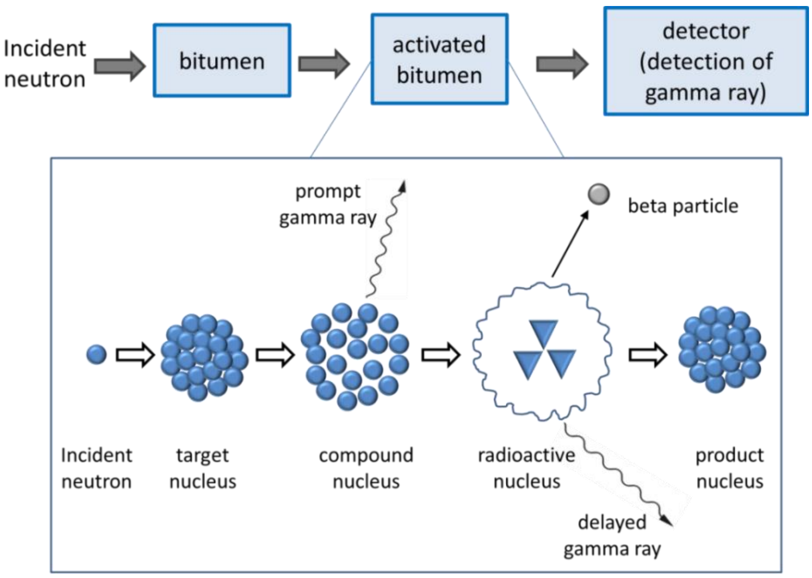

Figure 1: Schematic representation of Neutron Activation Analysis steps and illustration of the neutron capture process.

2.3 INAA facility and method of analysis

Bitumen samples were irradiated at the nuclear reactor and analyzed at the INAA facility of Reactor Institute Delft in TU Delft. The short-lived nuclides were analyzed by the 'SBP' (fast rabbit) facility and for the longer-lived nuclides; the irradiation and the measurements were carried out in the BP3 facility and 'SUR' detector respectively.

The analysis was performed by following three key steps: (i) sample preparation (ii) measurement and (iii) interpretation. Firstly, samples were prepared by taking a small amount of bitumen (~ 250 mg) by a spatula and placing them in separate polyethylene capsules. All samples were then sealed together with two additional capsules. Among these additional samples, one was filled with reference material (NIST SRM 1632c, Coal) and the other was an empty capsule (blank).

At first, this cluster of sample capsules was placed close to the core of the nuclear reactor in an irradiation container. A pneumatic irradiation tube system was used for transporting the capsules to a location of high radiation intensity, close to the reactor core. The samples were irradiated for 10s in a thermal neutron flux of approximately 1.82×10^{17} neutrons $m^{-2}s^{-1}$. Next, the samples were unpacked and the counting of short lived nuclides was immediately (7 minutes) carried out, for 5 minutes by the 'SBP' coaxial GeLi detector. Further, to determine the medium and long-lived nuclides, the batch of samples was irradiated (after 3 days) for an hour in a thermal neutron flux of approximately 4.24×10^{16} n $m^{-2}s^{-1}$. After 3 days of decay, the medium-lived nuclides were measured by 'SUR', a well type GeLi detector. And after 3 weeks of decay, the long-lived nuclides were measured using the same detector. After this third measurement, all three spectra of each sample are interpreted together using a UNIX-based computer system. The peaks are detected, their areas and energies determined, and the neutron flux is determined from the comparator spectra. Finally all these information is converted into a list of elements and their concentrations (*21*).

3. Experimental results and discussion

3.1 Results

The concentration of trace elements was obtained by INAA as described in the section above. From the detailed elemental analysis, it was found that each bitumen contained different sets of trace elements where the total number of elements varied from 17 to 28. The elements found in the materials studied are: sodium (Na), aluminum (Al), silicon (Si), chlorine (Cl), potassium (K), scandium (Sc), vanadium (V), chromium (Cr), manganese (Mn), iron (Fe), cobalt (Co), nickel (Ni), zinc (Zn), gallium (Ga), arsenic (As), selenium (Se), boron (Br), indium (In), antimony (Sb), iodine (I), barium (Ba), tungsten (W), rhenium (Re), gold (Au), lanthanum (La), cerium (Ce), samarium (Sm), ytterbium (Yb) and thorium (Th). Presence of these elements fingerprints the geochemical origin of the bitumen and of its crude oil source. Among all these trace elements in bitumen, vanadium, chromium, iron, cobalt, nickel and zinc are known to be the most abundant. Concentrations of these elements are presented in Table 1. Figure 2 shows a comparison of concentrations of the six abundant trace metals (V, Cr, Fe, Co, Ni, and Zn) in the original bitumen. Besides, the total concentrations of these metals are presented in Figure 3.

Table 1: Concentrations of the most abundant trace metals in bituminous materials

Bitumen samples	Most abundant trace metals in bitumen samples (ppm)					
	Vanadium (V)	*Chromium (Cr)*	*Iron (Fe)*	*Cobalt (Co)*	*Nickel (Ni)*	*Zinc (Zn)*
SHRP AAA-1	183±3.7	0.57±0.01	6.7±2	0.17±0.01	91.5±5.5	-
SHRP AAM-1	60.6±1.2	1.22±0.11	251.2±7.5	0.27±0.02	50.7±0.5	6.12±0.5
SHRP AAD-1	315.4±6.3	2.27±0.11	14.2±4.3	0.42±0.02	133.8±5.4	1.27±0.3
D-0114	126±2.5	-	21.9±2.8	0.20±0.01	27.3±3.0	0.94±0.2
D-0113	642.2±13	0.65±0.13	-	0.96±0.03	83.1±5.8	1.12±0.4
D-0184	629.0±12	0.36±0.11	12.8±3.9	0.94±0.03	79.3±7.1	0.58±0.2
B (20/30)	834.8±17	0.29±0.15	-	0.68±0.03	86.4±6.9	14.79±0.7
BNDM 90/130	62.7±1.3	-	13.2±2.7	0.26±0.01	38.5±2.7	1.11±0.2
BNDM 80/120	99.9±2.0	0.25±0.08	39±3.1	0.15±0.01	44.5±4.0	1.95±0.4
Fina 70/100	192.2±3.8	-	31.8±9.5	0.25±0.01	58.2±4.1	1.50±0.3
Fina 70/100+ 10% EVA	171.7±3.4	-	30.0±3.3	0.23±0.01	48.4±3.4	1.31±0.2
Fina 70/100+ 10% Sasobit	170.1±3.4	0.47±0.14	26.5±5.3	0.23±0.01	56.3±2.8	0.92±0.2
Sc-09-42 (40/60)	201.8±4.0	3.19±0.19	40.6±4.9	0.31±0.02	65.9±4.6	1.75±0.3

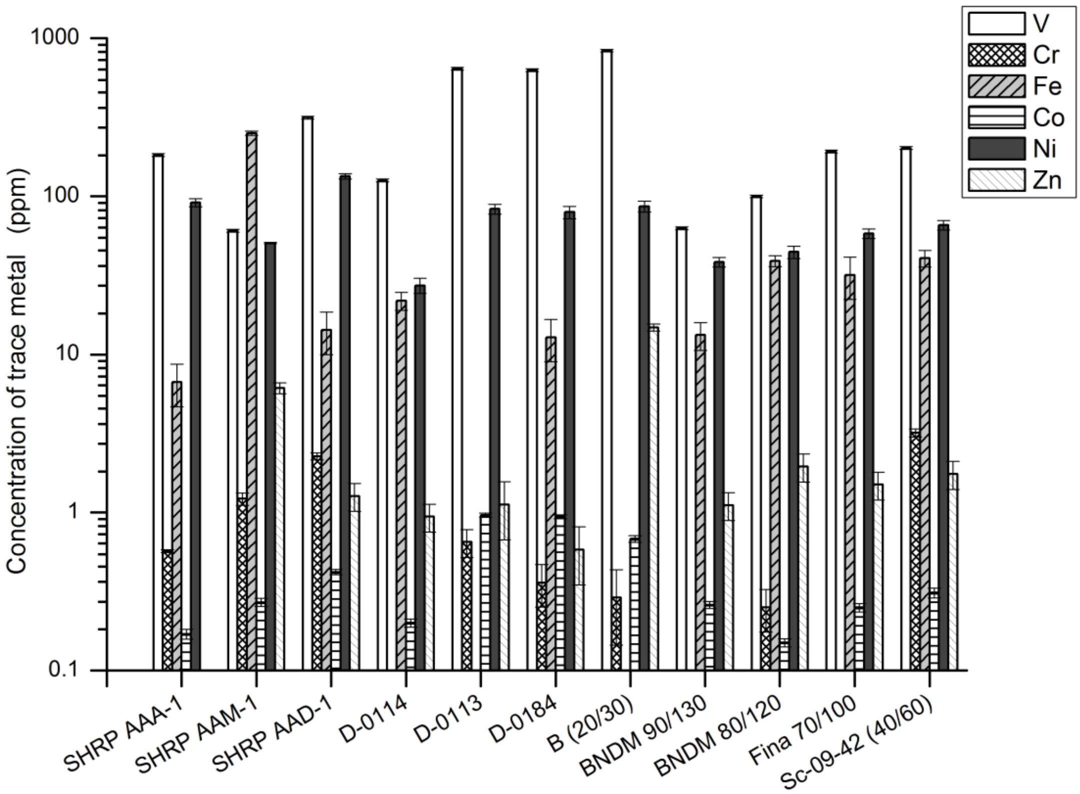

Figure 2: Concentrations of the most abundant trace metals, vanadium (V), chromium (Cr), iron (Fe), cobalt (Co), nickel (Ni) and zinc (Zn) in 11 pure bitumens.

Some key observations from the elemental analyses are summarized below:

- Vanadium, nickel and cobalt are present in all bitumens.
- Vanadium has the highest concentration that is in the range of 60 to 835 ppm. The next most abundant element is nickel and it is present in concentrations from 25 to 135 ppm.
- Iron is commonly present at concentrations below 50 ppm in all bitumens, except AAM-1. This bitumen is very rich in iron with an average concentration of 250±7 ppm. Bitumen D-0113 and B (20/30) do not contain any detectable amount of iron.
- Zinc is present in all bitumens except AAA-1. The concentration ranges from 1 to 15 ppm where in most cases it is below 2 ppm. The maximum amount of zinc (15 ppm) is present in B (20/30).
- Chromium is present in concentrations from 0.3 to 3 ppm in 7 bitumens and in one modified bitumen (Fina 70/100+ 10% Sasobit). And no chromium is detected in bitumen D-0114, BNDM 90/130 and Fina 70/100. As the fresh bitumen Fina 70/100 doesn't contain any chromium, it is possible that the source of measured chromium can be the additive, Sasobit.
- Cobalt is present in all bitumens at low concentrations (0.15 to 1 ppm).

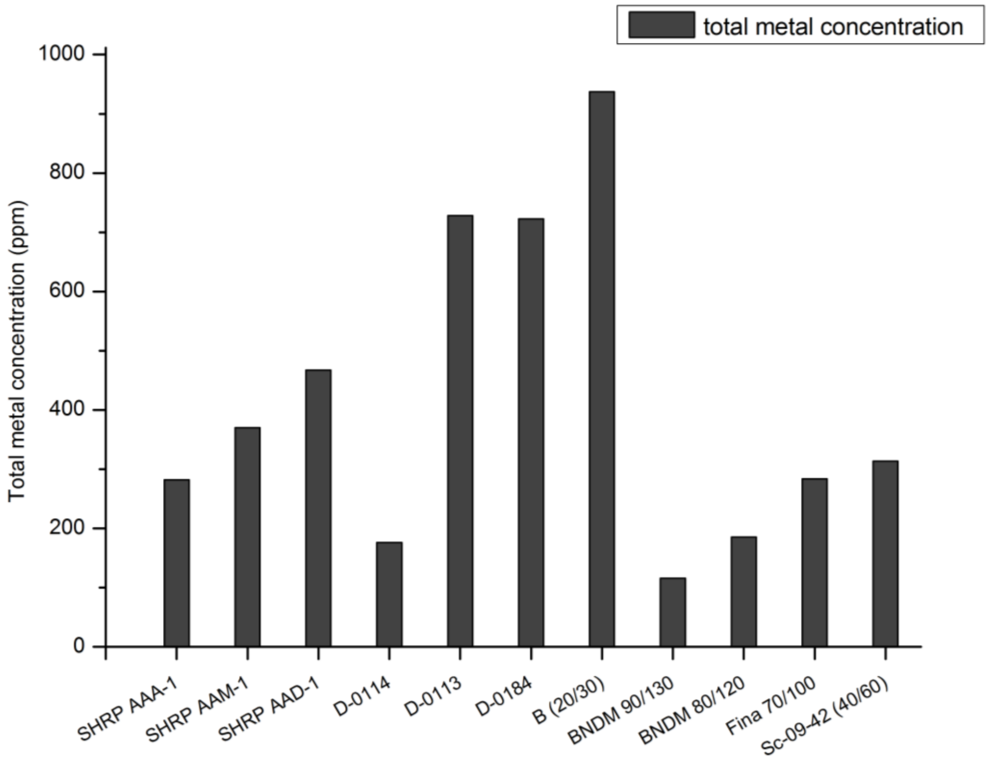

Figure 3: Total concentrations (ppm) of the most abundant trace metals, vanadium (V), chromium (Cr), iron (Fe), cobalt (Co), nickel (Ni) and zinc (Zn) in 11 pure bitumens.

- The total amount of INAA-detectable metals in all pure bitumens is presented in Figure 3. Bitumen D-0113, D-0184 and B (20/30) are very rich in total metal, especially vanadium and nickel occur in relatively high concentrations. Bitumen D-0114, BNDM 90/130 and BNDM 80/120 possess only a small concentration (< 200 ppm) of metals. The total metal content is a good indicator for the susceptibility of the material to aging (*23; 24*).
- The concentration of specific trace metals in bitumen can be a guide to the petroleum source. For example, bitumen D-0113, D-0184 and B (20/30) are very rich in vanadium

and nickel content. The Venezuelan crude oil is commonly known as rich in vanadium content and bitumens from Peru, Argentina and Venezuela have high nickel content (*10*). Once the link between the trace-metal content and the crude sources is established, one can reveal the source of the petroleum.

3.2 Common trace elements in SHRP bitumens

There are 16 trace elements commonly present in all three SHRP bitumens (AAA-1, AAM-1, AAD-1) and their concentrations are presented in Table 2. Among these common elements, the most abundant trace elements are: vanadium (60 to 315 ppm), nickel (51 to 134 ppm) and iron (7 to 251 ppm). Whereas, antimony and rhenium are present at very low concentrations. The concentrations of antimony and rhenium range from 20 to 60 and 3 to 40 ppb respectively in SHRP bitumens.

Table 2: Concentrations of common trace elements of three SHRP bitumens by INAA

Common elements in SHRP Samples	**Concentration of trace elements (ppm)**		
	AAA-1	*AAM-1*	*AAD-1*
Sodium (Na)	12.40±0.12	13.90±0.28	29.80±0.27
Aluminum (Al)	2.10±0.42	11.80±0.59	2.20±0.44
Chlorine (Cl)	16.00±3.2	8.00±2.4	49.00±3.92
Vanadium (V)	183.00±3.66	60.60±1.21	315.00±6.3
Chromium (Cr)	0.57±0.11	1.22±0.11	2.27±0.11
Iron (Fe)	7.00±2.1	251.00±7.53	14.00±4.2
Cobalt (Co)	0.17±0.01	0.26±0.02	0.42±0.02
Nickel (Ni)	92.00±5.52	51.00±5.61	134.00±5.36
Gallium (Ga)	0.26±0.03	0.07±0.02	1.52±0.03
Arsenic (As)	0.18±0.005	0.42±0.008	0.08±0.005
Selenium (Se)	0.38±0.038	0.26±0.05	0.49±0.005
Bromine (Br)	0.12±.008	0.27±0.01	0.40±0.02
Molybdenum (Mo)	7.44±0.15	0.19±0.04	3.14±0.13
Antimony (Sb)	0.02±0.004	0.06±0.005	0.05±0.005
Rhenium (Re)	0.04±8E-4	0.003±9E-4	0.03±9E-4

There are total 19 different trace elements present in AAA-1 with the total amount of 282 ppm. AAM-1 has 28 trace elements with total concentration 370 ppm. AAD-1 has the highest total concentration; i.e., 468 ppm from 20 elements. Gold (Au), zinc (Zn), thorium (Th) are absent in AAA-1, however ytterbium (Yb) is only present in this material. Besides, scandium (Sc) and samarium (Sm) are absent in AAD-1 and tungsten (W) is only found in this bitumen. AAM-1 contains additional 7 elements and they are potassium (5.1 ppm), barium (7 ppm), lanthanum (0.076 ppm), cerium (0.11ppm), manganese (0.91 ppm), indium (0.03 ppm) and iodine (0.7 ppm).

3.3 Comparison of concentrations of trace metals (V, Ni, Fe) in SHRP bitumens measured by different techniques

The trace metals determined by INAA are compared to existing data reported in SHRP program for SHRP bitumens: AAA-1, AAM-1 and AAD-1 (*25*). In SHRP program, only three most abundant trace metals, vanadium, nickel and iron were measured by inductively coupled plasma emission spectrometry (ICP) (*18*). The comparison of the concentrations is made between these two sets of measurements in Figure 2. The concentration of each metal measured by the individual techniques are found to be the same, with small deviation. However, to probe lower concentrations, INAA is far more sensitive (e.g. iron concentration of bitumen AAA-1).

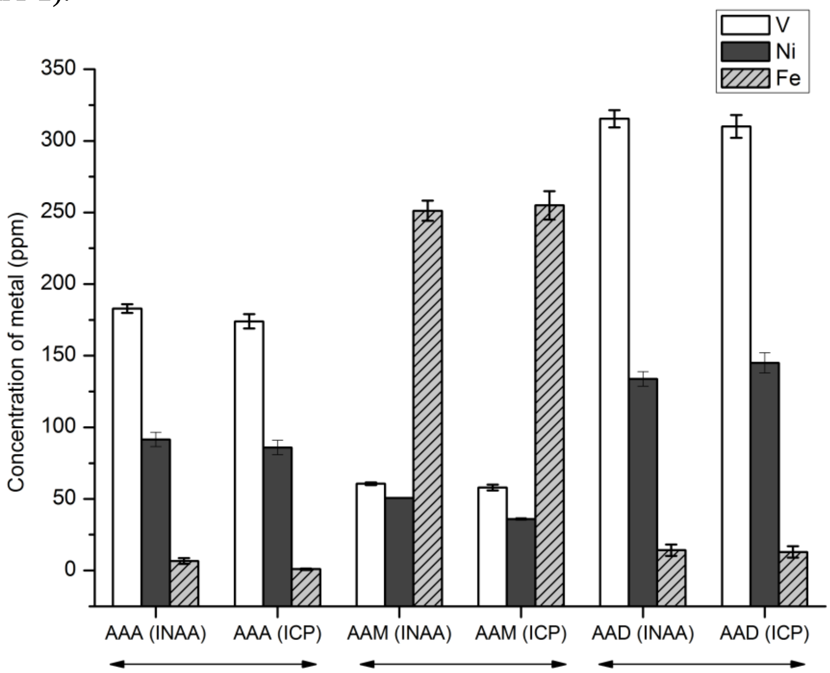

Figure 4: Comparison between concentrations of trace metals measured by INAA and ICP in SHRP program for bitumens: AAA-1, AAM-1 and AAD-1.

The concentrations of the most abundant trace metals measured by INAA, the concentrations of the hetero elements (N, O, S) and asphaltene fractions of the SHRP bitumens are presented in Table 3. Here, the metals are known to be associated with the asphaltene fraction of bitumen in the form of porphyrin like organometallic complexes in which the metallic cations are bonded to the hetero atoms (*1; 5; 6; 10*).

Table 3: Hetero elements, trace metals and asphaltene content in SHRP Bitumens

SHRP Sample	Hetero elements* (w/w %)			Asphaltene* (w/w %)	Trace metals by INAA (ppm)			
	Nitrogen N	*Oxygen O*	*Sulphur S*	*n-heptane*	*Vanadium V*	*Nickel Ni*	*Iron Fe*	*V+Ni*
AAA-1	0.5	0.6	5.5	16.2	183±3	92±5	7±2	275
AAM-1	0.55	0.5	1.2	4	61±1	51±0.5	251±7	112
AAD-1	0.77	0.9	6.9	20.5	315±6	134±5	14±4	449

*Data source: report: SHRP-A-645 (*25*)

From Table 3, it can be outlined that asphaltene content, trace metals and hetero atoms, especially sulphur, exhibit good correlations. High amount of vanadium and nickel containing bitumen is usually rich in asphaltene. AAD-1 possesses the highest amount of vanadium and nickel (449 ppm) and it has the maximum asphaltene fraction of 20.5% (w/w). The next bitumen, rich in metals (275 ppm) is AAA-1 and contains 16.2% (w/w) asphaltene. AAM-1 has the least vanadium and nickel concentration of 112 ppm as well as the asphaltene content (4% w/w). However, a high concentration of iron (251ppm) is detected in AAM-1 by INAA and the same is also characterized in SHRP program by using ICP technique (255ppm). Besides, it is observed that, the higher the sulphur content in any bitumen, the larger the asphaltene fraction. In the case of sulphur concentration, the SHRP bitumens follow the same order of the total amount of vanadium and nickel (AAD-1> AAA-1> AAM-1).

3.4 Consistency in trace metal concentrations measured by INAA

The consistency of INAA data can be checked from the metal concentration of Fina 70/100 and its derived modified bitumens Fina 70/100 + 10% EVA and Fina 70/100 +10% Sasobit. The comparison data is presented in Figure 4 and Table 4. Both modified bitumens (10% w/w) showed 90% vanadium content of the original bitumen Fina 70/100. But minor inconsistency is observed in nickel and iron concentrations of modified bitumens. Bitumen Fina 70/100+10% EVA has 83% nickel concentration relative to the pure bitumen. Whereas, Fina 70/100+ 10% Sasobit contains 96% nickel content relative to pure Fina 70/100 (higher than the pure bitumen). Concentration of iron in Fina 70/100+ 10% EVA is 94% and in Fina 70/100+ 10% Sasobit is 83% of the original bitumen.

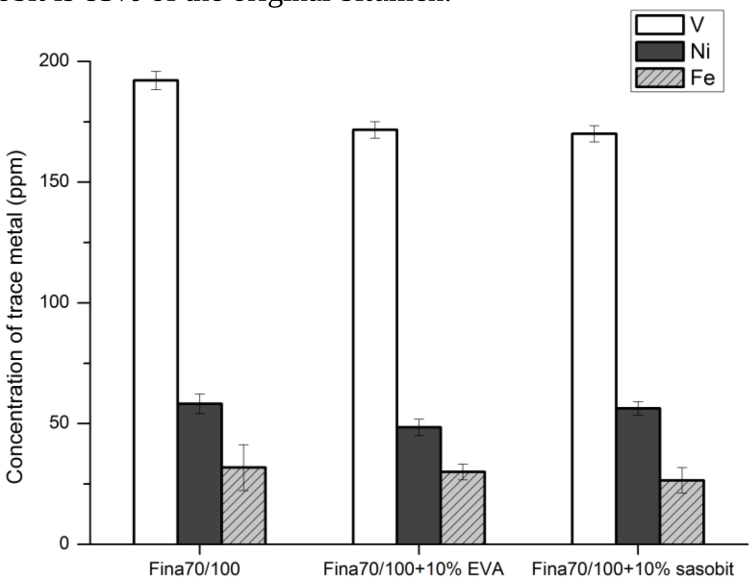

Figure 5: Consistency in concentrations of trace metals measured by INAA.

This inconsistency in trace metal content may have two possible sources. The additional amount of nickel (1.2 ppm) in Sasobit and iron (3.4 ppm) in EVA modified bitumen may have originated from the possible impurities of EVA and Sasobit respectively. It is plausible that these industrial grade additives contain some foreign metals at very low concentrations. The depreciation of 4 ppm nickel and 2.2 ppm iron can be the consequences of inhomogeneity of the additive within the material. As small amount of sample (~ 250 mg) is measured by INAA, material homogeneity (specially for modified binder) can influence the data obtained. If a small amount of these metals are present in unbound form in bitumen, it can also be a source of such inconsistency.

Table 4: Consistency of trace metal concentrations measured by INAA.

Bituminous materials	**Concentration of trace metals (ppm)**			**Comparison of concentrations (consistency)**		
	Vanadium V	*Nickel Ni*	*Iron Fe*	*Vanadium V*	*Nickel Ni*	*Iron Fe*
Fina 70/100	192.20±3.8	58.21±4.1	31.76±9.5	V_o	Ni_o	Fe_o
Fina 70/100+ 10% EVA	171.70±3.4	48.44±3.4	30±3.3	0.90V_o	0.83 Ni_o	0.94 Fe_o
Fina 70/100+ 10% Sasobit	170.10±3.4	56.31±2.8	26.47±5.3	0.90V_o	0.96 Ni_o	0.83 Fe_o

V_o, Ni_o, Fe_o = concentrations of vanadium, nickel and iron in pure Fina 70/100

4. Conclusions

The concentration of the trace elements in eleven pure bitumens and two modified bitumens have been successfully obtained by neutron activation analysis, INAA. By using this technique, a complete trace elemental map is obtained for each bitumen. This elemental analysis shows the characteristic chemical signature of bitumens from different crude oil sources. The complete analysis can be performed at relatively low cost (estimation of commercialized INAA analysis is a few hundred dollars per bitumen sample).

From the analyses of SHRP bitumen, it is concluded that trace metals correlate well with the hetero atoms in bitumen, especially sulphur. Vanadium and nickel rich bitumens are known to contain high amount of sulphur which is also observed in this study (*23*). AAD-1 is characterized by its high metal concentration of 468 ppm and it also contains a higher fraction of sulphur (6.9%) compared to the other SHRP bitumens.

The asphaltene fraction of bitumen hosts most of these metals. The metals play an important role in the structure of asphaltene molecule. The type and concentration of metals also influences the asphaltene molecular association and aggregation characteristics. The size and structure manipulates the dispersion of these particles within the matrix of the material and controls the rheology. In this way metal content correlates with the rheological properties of bitumen. Furthermore, total metal concentration correlates with the asphaltene fraction. The SHRP bitumen (AAD-1) that is richest in metals, also has the highest asphaltene fraction (20.5% w/w, n-heptane).

Concentrations of trace metals, especially vanadium and nickel, are good indicators for bitumen aging propensity (*10; 17; 19; 26*). These metals are present mainly in two forms in asphaltenes, i.e. porphyrinic and non-porphyrinic (*6*). Branthaver et al. (*23*) investigated the effect of metallo-porphyrins on bitumen oxidation and concluded that vanadyl porphyrins can promote bitumen oxidation, while nickel porphyrins show less or no activity in oxidation. The type of metal and its porphyrinic and non-porphyrinic fractions mainly govern the propensity of bitumen to oxidation. However, the correlation of the metal concentration in bitumen and its susceptibility to oxidation is not straightforward. The apparent reason is that the molecular make up in bitumen varies from source to source and that introduces different amounts and types of oxidizable molecules. From a physico-chemical point of view, the relation between trace metal content and ageing characteristics of bitumen, is not that surprising. The most abundant trace elements in bitumen are so-called transition metals. These transition metals have the property that they can occur in many different oxidation states. For instance Vanadium can occur as V^{2+}, V^{3+}, V^{4+}, V^{5+}, and iron, also a transition metal occurs in oxidation states Fe^{2+} and Fe^{3+}. Thus, these transition metals can easily donate or accept electrons, therefore there use in batteries and as catalysts. But exactly these electronic properties of transition metals will play a role in the various ageing scenarios in bitumen.

In this study, bitumen D-0113, D-0184 and B (20/30) are found very rich in total metal content (i.e., vanadium and nickel). From literature, especially petroleum geochemistry, it is known that trace metal content is a good predictor of petroleum origin, age and migration. In the future, systematic investigations of a broader material library can provide more information on metal content and the respective material source. Once such knowledge is available and a link is established, one can trace back the source of bitumen from its metal constituents.

Vanadium and nickel concentration in bitumen can provide a general idea on aging susceptibility of the material. But more research is required to understand clearly these oxidative pathways in relation to metal concentration. Another possible application of the method can be the identification of the original bituminous ingredients in recycled asphalt pavement (RAP) or recycled asphalt shingles (RAS) in a stock pile. By extracting the bitumen from the RAP or RAS and carrying out the neutron activation analysis, a chemical signature of the bitumen and the original bitumen source can be obtained. Again from the analyses of the modified binders, it is proposed that, it can be a tool for the future characterization of homogeneity of additives to the bitumen matrix in different modified binders.

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