DETERMINATION OF THE CORRELATION BETWEEN ELEMENTAL AND ORGANIC CARBONS TO TRACE ELEMENTAL SUBSTANCES AND ANIONS IN DPM SAMPLES

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ABSTRACT:

The focus of the entire project is to characterize diesel particulate matter from various mining commodities into its respective constituents and to further evaluate and outline the possible identified markers for better health engineering improvements and analysis techniques. Samples investigated were received from different mine commodities and were initially characterised for their diesel particulate matter content and trace elemental substances on a thermo-optical analyser and an inductively coupled plasma instruments respectively. For this phase of the project, the same samples were further analysed on a photometric anion analyser (Gallery instrument) for their respective anions constituents. The objective of this phase was to identify the correlation and possible effects of the concentrations of the diesel particulate matter (on elemental carbon EC and organic carbon OC), trace elemental substances and the measured anionic substances found in the diesel particulate matter samples that were investigated. Seven major anions were investigated and, the chloride, ortho-phosphate and sulphate anions were detected. An assumption was made for two samples V03 and V04 that a correlation exists between the detected diesel particulate matter (on elemental carbon EC and organic carbon OC) contents, trace elemental substances and the anions. Sample V03 indicated the presence of impurities such as sulphates, iron, zinc and sodium in the fuel used while sample V04 indicated a contamination such as phosphates due to wear and tear. However, the presence of some of the analytes in the samples was assumed to could have been contributed by the sampling environment.

1   INTRODUCTION

Diesel particulate matter (DPM) is a result of the incomplete combustion of diesel fuel in motor vehicles and other diesel machinery. This DPM is released as part of the exhaust gas which is formed by a mixture of poly-aromatic hydrocarbons (PAHs) and soot aerosol [6]. DPM is, thus, a cluster of ultra-fine diesel particulate matter that has particle sizes of not greater than 3 microns. This particle size renders them very light and often invisible by the naked human eye such that they can travel long distances in the air and still be inhaled by living organisms.

Due to their respirable nature and toxicity as proven by previous studies [8], they therefore, pose a health hazard in the lives of humans and animals. In the previous years, a number of studies have been conducted by various health institutions and co-workers to determine the definite composition of the exhaust [8]. PAHs and soot particulate matter including non-organic compounds such as sulphates were discovered in some of these studies [10]. The PAHs form the main gas-phase of the released exhaust gas while the soot-particulates form the particulate matter (PM) of the released gas. Previous studies [10] revealed that soot is composed of ultra-fine particulates called diesel particulate matter (DPM) which is coated with a layer of the toxic amounts of PAHs.

As mentioned in the NIOSH 5040 method for the sampling and analysis of DPM, the samples are collected on tissue quartz fibre filters [5]. Very little or no elements should be present in DPM since the source of this exhaust gas involves the raw material diesel fuel and carbon spark. Temperatures in the engine combustion chamber can as high as 700 °C which can only destroy a few elements than most. Before this fuel is used, analytical testing is carried out to determine factors such as the flash point and the amounts of impurities present to see if whether they meet their specifications. Very few metal elements are often found in the fuel [3].Aliquots of samples used in this study were taken from diesel particulate matter (DPM) samples, previously prepared and analysed for trace elemental substances [21].

The samples were initially acquired from the platinum, gold, copper, chrome and coal mining sectors. An additional sample was acquired from a workshop where diesel fuel testing was being conducted from various concentrations of sulphur (S) contents in the diesel fuels. Table 1 lists the different commodities that were initially investigated for diesel particulate matter content (EC/OC) and trace elemental substances.

Table 1: Sample numbers and commodity mine source

Sample number	Commodity
Blank	Blank filter
V01	Platinum mine A
V02	Platinum mine B
V03	Platinum mine B
V04	Copper
V05	Coal
V06	Gold mine A
V07	Gold mine B
V08	Gold mine B
V09	Controlled environment
V10	Chrome

The above listed diesel exhaust samples were acquired as particulate exhaust fumes distributed and adsorbed on 37 mm tissue quartz fibre filters. The purpose for this type of sample handling was to allow light gas fumes whose particle and molecular sizes are less than 2.2 µm in diameter to pass through the filter but trap particulates of the fumes that are greater than the 2.2 µm diameter size. These filters can withstand temperatures as high as 1093 ^{0}C without decomposing. They also have very low levels of alkaline earth metals imbedded in them as well as very low possibilities of formation of by-products of sulphates and nitrates as a result of the reactions with the filter during sampling as described by their manufacturer.

Figure 1 below depicts the results of DPM (EC and OC) obtained during the analysis of the samples used in this phase of the project.

The filters of these samples were punched an area of 1.5 cm^2 per filter and analysed for DPM on a thermo-optical analyser instrument.
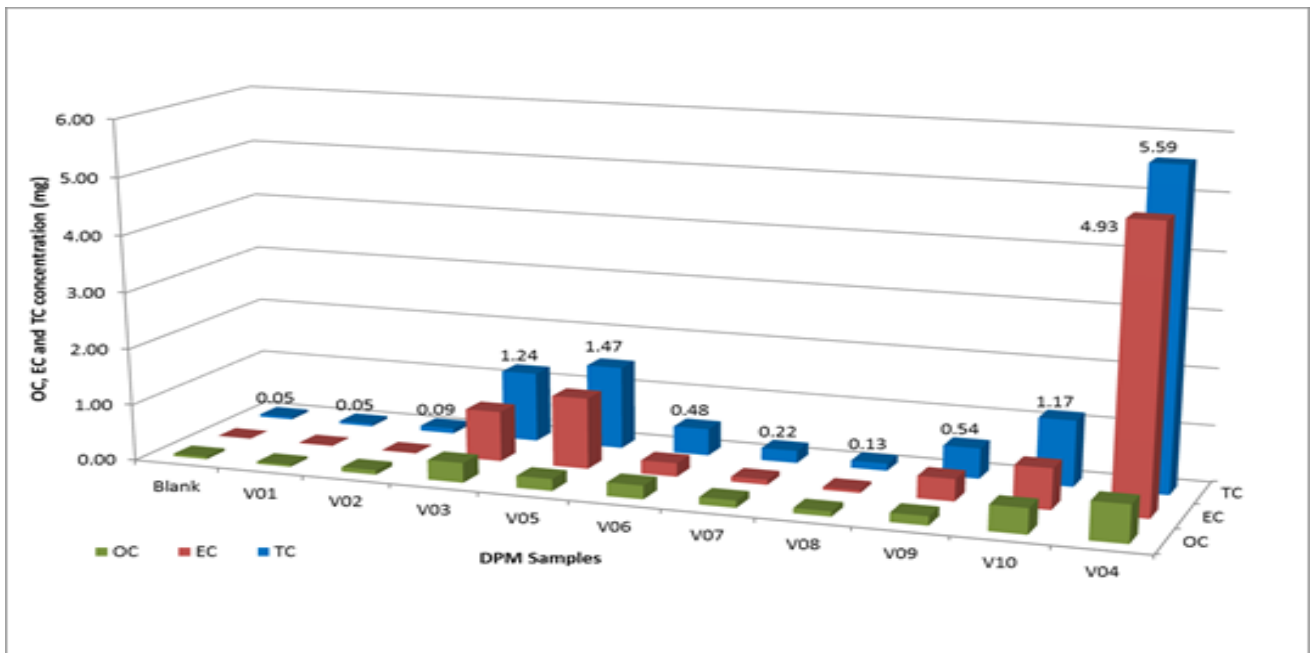
Figure 1: The results obtained for DPM analysis on elemental carbon (EC) and organic carbon (OC)

For trace elemental analysis on these samples, they had to be first put into solution through a digestion with acids. Once dissolved, the samples could easily be aspirated into instruments such as the inductively coupled plasma (ICP), the atomic absorption spectroscopy (AAS) and Ion-chromatography (IC).

In this case the digestion process involved the use of concentrated hydrochloric acid (HCl) to decompose the amorphous carbon ash and concentrated nitric acid (HNO_3) to dissolve the metals. Premised on the argument based on the results obtained from the analysis of these samples for trace elemental substances, the samples were screened for a variety of elemental substances thereof which only the concentrations of 17 elements were found to be above elemental detection limits of their analytical methods. These elements include: silver (Ag), aluminium (Al), calcium (Ca), chromium (Cr), copper (Cu), iron (Fe), magnesium (Mg), potassium (K), sodium (Na), strontium (Sr) and zinc (Zn). The concentration levels of these elements are presented in Fig. 2.
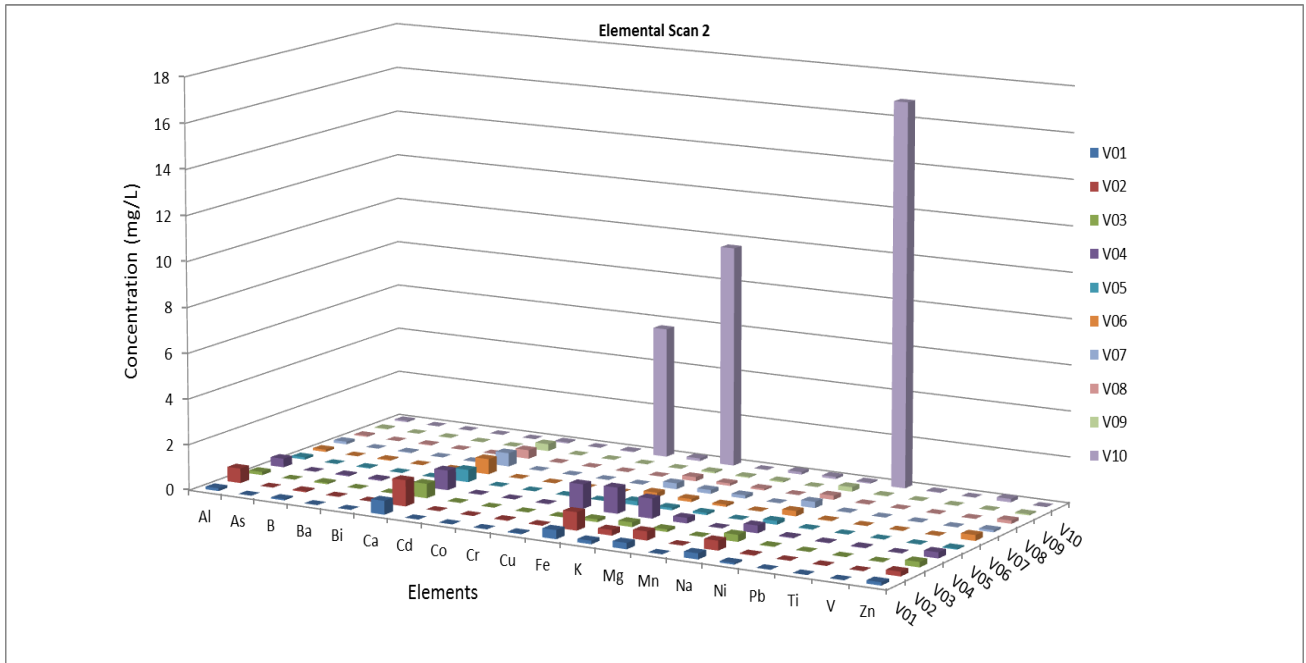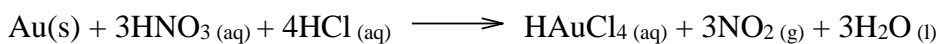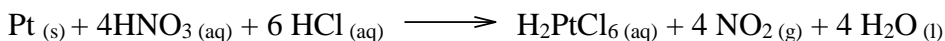
Figure 2: The results obtained from the trace elemental determinations in the DPM samples

Basic chemistry clarifies that certain metals such as copper (Cu), mercury (Hg), gold (Au) and silver (Ag) do not react in hydrochloric acid since the reduction potential of these elements is higher than that of the solvent acid. But this occurs with pure metal substances of the above elements and not their oxides [9].

In normal typical extractions of gold (Au), platinum (Pt) and other metal substances, an aqua-regia is the most powerful displacement solvent to be used. This is a mixture of concentrated HNO_3 and HCl optimally mixed in the ratio of 1:3, respectively [11].

Typical reactions of metals with aqua regia are known to occur as follows:

$$Pt_{(s)} + 4HNO_{3\,(aq)} + 6\,HCl_{(aq)} \longrightarrow H_2PtCl_{6\,(aq)} + 4\,NO_{2\,(g)} + 4\,H_2O_{(l)}$$

$$Au_{(s)} + 3HNO_{3\,(aq)} + 4HCl_{(aq)} \longrightarrow HAuCl_{4\,(aq)} + 3NO_{2\,(g)} + 3H_2O_{(l)}$$

The chemistry applied during this phase of the project involved a split digestion. In this process, the samples were initially subjected to concentrated hydrochloric acid without any other medium involved. Heating was applied to evaporate the acid. Normal reactions of chloride acids with metal oxides are known to produce chloric salts of the metals. This was then applied as the assumption in this process. The reason for this step in the digestion process of the samples was, to first decompose the sample matter but be able to completely remove the acid material through heating the mixture to a temperature above the boiling point of HCl.

Hydrochloric acid (HCl) is corrosive to instrument materials it would therefore be necessary to decompose the samples and immediately remove the HCl solvent as mentioned above. Many ores and minerals dissolve in hydrochloric acid, this includes, sulphides, phosphates, carbonates, borates and some oxides and silicates. However, this is an exception in certain cases for some pure elements that are below the reactivity potential of hydrogen (H). The hydrogen ions (H^+) would not be displaced from their chloride ion (Cl^-) by any substance of higher reduction potential than what is has (+0.0V). This is therefore the case with silver (Ag) at +0.80 volts, gold (Au) at +1.5 volts, platinum (Pt) at +1.2 volts, mercury (Hg) at +0.86 volts and copper (Cu) at +0.52 volts as pure metals [4].
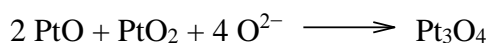
The following would be typical reactions that would take place between the sample materials and the concentrated hydrochloric acid:
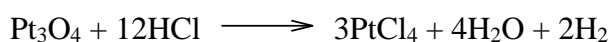
$$Au_2O_3 + 6HCl \longrightarrow 2H[AuCl_4] + 3H_2O$$
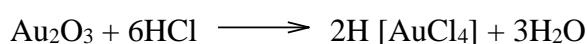
The main product of interest from the above is $[AuCl4]^{2-}$

[The form of Au^{+3} (+1.5v) would be soluble in HCL but not Au^+ (+1.68v)]

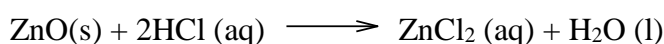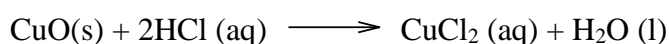Platinum (IV) oxide is produced under heat in the following manner:

$$2\,PtO + PtO_2 + 4\,O^{2-} \longrightarrow Pt_3O_4$$

The Pt_3O_4 will then be subjected to the chloride acid.

$$Pt_3O_4 + 12HCl \longrightarrow 3PtCl_4 + 4H_2O + 2H_2$$

[Both chloride forms of Pt^{+2} and Pt^{+4} would also be soluble in HCl]

$$CuO(s) + 2HCl\,(aq) \longrightarrow CuCl_2\,(aq) + H_2O\,(l)$$

$$ZnO(s) + 2HCl\,(aq) \longrightarrow ZnCl_2\,(aq) + H_2O\,(l)$$

The second step of the digestion procedure involved the reaction of concentrated nitric acid with the produced chloride salts (Cl^-) of the products of HCl and the metal oxides. The assumption was that the hydrogen ions (H^+) would displace the other elements at different reaction ratios, a form of ion exchange. It is however known that the latter does not occur with chromium salts (Cr^+, Cr^{2+}, Cr^{3+}, Cr^{4+}, Cr^{5+} and Cr^{6+}) since they are fairly insoluble but dissociates under heating. Most common forms of the insoluble chromium are chromium (III) being Cr^{3+}, chromium (IV) as Cr^{4+} and chromium (VI) as Cr^{6+} [7].

Typical reactions for the assumption above would be as follows:

$$CuCl_2 + HNO_3 \rightleftharpoons Cu(NO_3)_2 + Cl_2 + H_2O$$

$$CrCl_3 + HNO_3 \rightleftharpoons Cr(NO_3)_2 + Cl_2 + H_2O$$
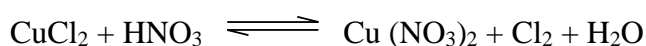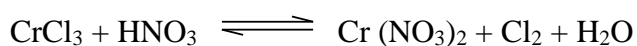
The reaction of $CrCl_3$ with HNO_3 favours the products due to higher relative entropy of the products.

The products of the above sample reactions produced the results presented in Fig. 2 for trace elemental analysis. The remainder of the prepared samples were also analysed using a photometric analyser (Gallery instrument) for their anions contents. Generally, to determine anions in liquids, the samples need very little or no treatment at all except filtration such that they do not clog the instrument sample lines. In this case, the samples were already treated from solid forms of DPM on adsorbed on to filter papers into liquid forms. The assumption was that the presence of anions such as chlorides (Cl^-) and nitrates (NO_3^-) in the acids would contribute largely to the chloride and nitrate ions in the samples

2   METHODOLOGY

Ten DPM samples initially analysed for elemental and organic carbon then for trace elemental substances were taken and analysed for anions on a photometric analyser. The used samples were initially prepared for trace elemental analysis using the HCl and HNO_3 digestive solvents that incorporated anions such as chlorides (Cl^-) and nitrates (NO_3^-). The samples were analysed on a photometric analyser (Gallery instrument) for various anions including fluorides (F^-), nitrites (NO_2^-), nitrates (NO_3^-), chlorides (Cl^-), ammonia (NH_3), ortho-phosphates (PO_4^{2-}) and sulphates (SO_4^{2-}). The objective of these determinations was to investigate the correlation between the EC/OC content to that of the trace elemental substances and their anions substances found in each DPM sample analysed.

3   RESULTS AND DISCUSSION

Anionic substances found in DPM measured using the Gallery Photometric analysers are presented here below.

Table 3: Results of anionic substances found in DPM measured using a Gallery Photometric analyser

Analytes determined in ppm (mg/L)	
Item	
1	Ammonia (NH_3)
2	Chlorides (Cl^-)
3	Fluorides (F^-)
4	Nitrites (NO_2^-)
5	Nitrates (NO_3^-)
6	O-phosphate (PO_4^{2-})
7	Sulphate (SO_4^{2-})

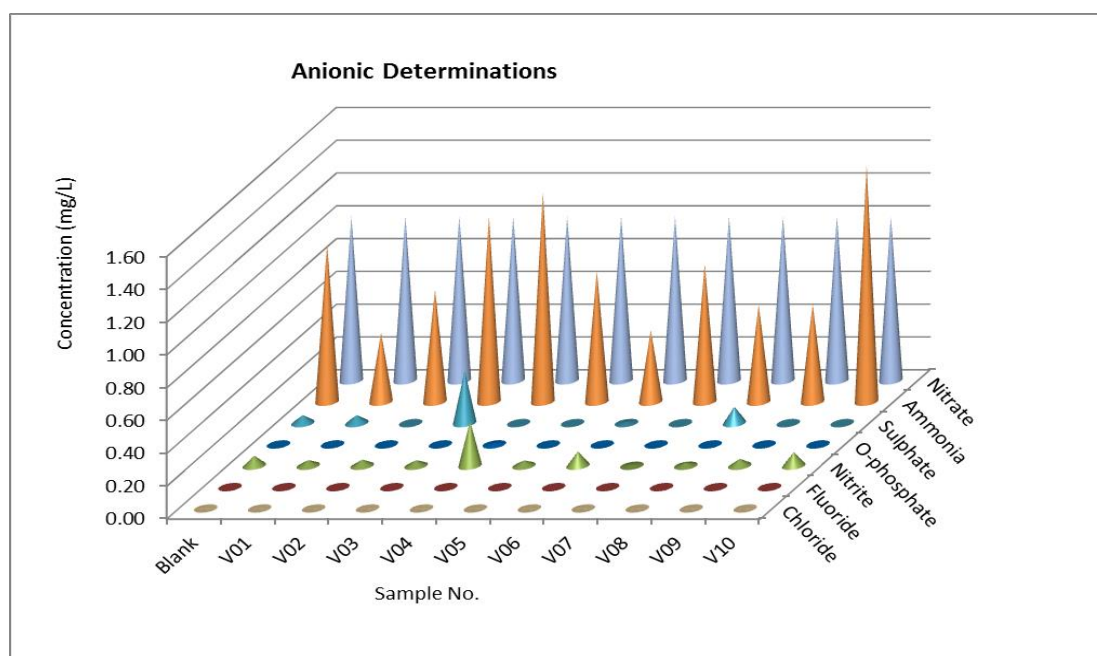The following substances were determined as presented in (Fig. 3):

Figure 3: The graphical representation of the raw results of anions

Seven major anions were investigated during this experiment. They included ammonia (NH_3), Chlorides (Cl^-), fluorides (F^-), nitrite (NO_2^-), nitrate (NO_3^-), phosphates (PO_4^{2-}) and sulphates (SO_4^{2-}).

It was described in the introduction section that the reagents used during the digestion, contained NO_3^- and Cl^-. The assumption is that these reagents could introduce or contribute to the presence of NO_2^-, NO_3^- and NH_4^+ in the samples. Hydrogen chloride (HCl) has a boiling point of 57 ^0C and breaks down giving mixtures of H^+, H_2, Cl^-, Cl_2 and HCl. The hydronium ions are assumed to react

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with some of the substances in the sample while some of them will diatomize and evaporate as hydrogen gas. The chlorides will also react with some of the materials in the sample and some of them will diatomize and break away as chlorine gas. Figure 4 represents the results of the anions investigated where the blank values were subtracted from the raw results obtained.
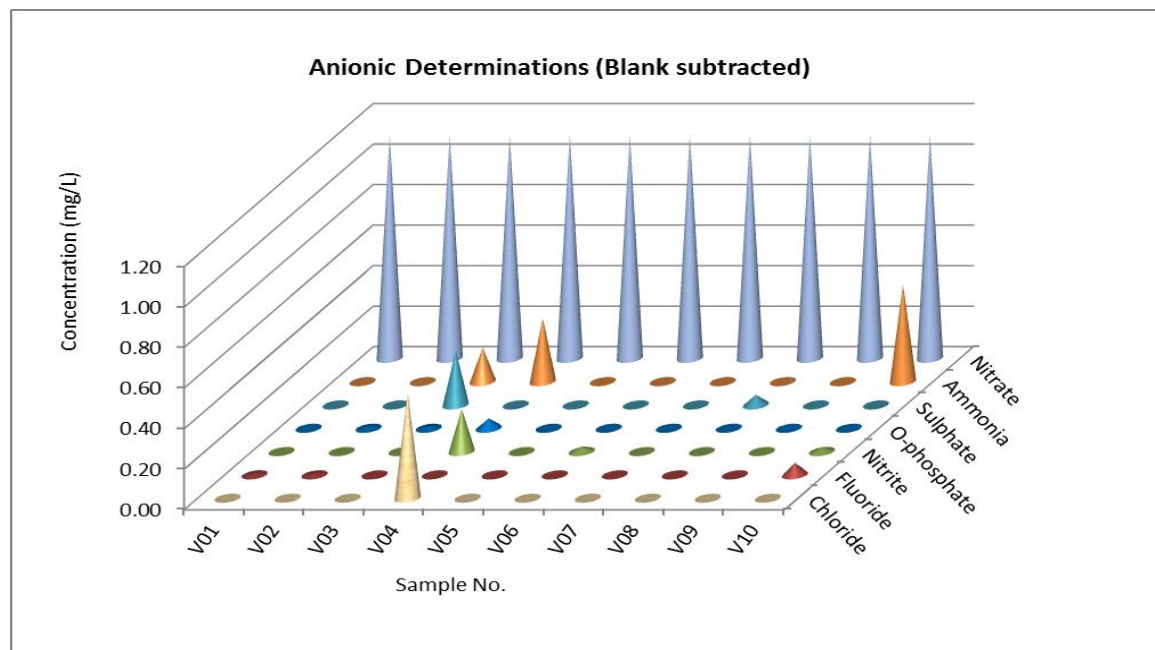

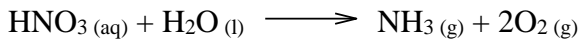Figure 4: The graphical representation of the results of the anions after blanks were subtracted

During the determinations, NO_3^- was found to be above the analytical range of the detector, thus, flooded the detector. Since concentrated HNO_3 was used in the second step during the digestion process of the samples, though most of it may have decomposed to NO and NO_2 and evaporated as nitrogen dioxide (NO_2), water (H_2O) and oxygen (O_2) but some of it reacted with the metal salts substituting the chloride ions (Cl^-) from their substrates with nitrates (NO_3^-). The thermal decomposition process can be presented as follows:

$$4HNO_{3\,(aq)} \longrightarrow 2H_2O + 4NO_{2\,(g)} + O_{2\,(g)}$$
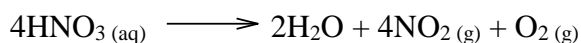
Some of the nitrate anions would also undergo loss of electrons and form the unstable nitrite compounds (NO_2^-) with the sample materials. As a result, the NO_2 and NO_3 anions cannot be considered in this determination even though the nitrite may have only been affected to a little extent.

A large amount of ammonia was also detected from these samples including the blank; apart from the known fact that some engines fitted with selective catalytic reduction catalysts (SCR) could aid

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to the presence of ammonia in the samples, these must have been a contribution of nitrogen and hydrogen from the heated reaction of the decomposing nitric acid with its water product to form ammonia and oxygen as shown in the following reactions:

$$HNO_{3 (aq)} + H_2O_{(l)} \longrightarrow NH_{3 (g)} + 2O_{2 (g)}$$

$$2HNO_{3 (g)} \rightleftharpoons NO_2^+ + NO_3^- + H_2O_{(l)}$$

Excluding the three anions, ammonia (NH_3), nitrites (NO_2^-) and NO_3^-), four analytes remained and are presented in the graph below.
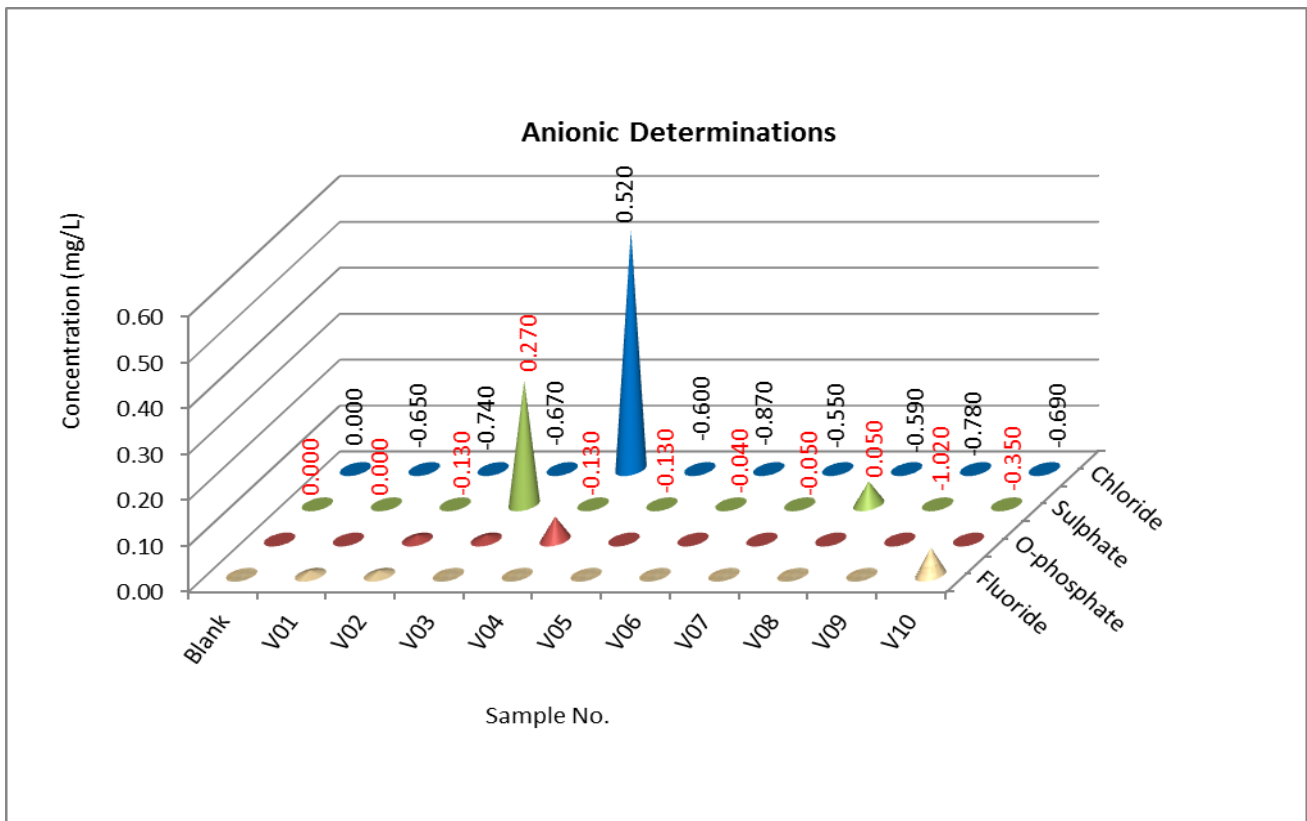

Figure 5: The graphical representation the results of the four remaining anions

Sulphate appears in samples V03 and V08 with a huge amount detected in sample V03. Sulphates are known to be as a result the conversion of sulphur oxides coming from both the engine oil additives and escaping into the combustion chamber and as well as the sulphur oxides from the diesel fuel. These conversions lead to the acidic formation of the sulphate acids in the engine. A little amount of phosphate and fluoride ions were found in samples V04 and V10 respectively. The phosphate in sample V04 can be attributed to the diesel engine oil anti-wear agents such as zinc di-thiophosphate (ZDDP) and corrosion inhibitors [22]. The presence of sulphates and phosphates in a sample could be an indication of a poisoned engine`s catalytic convertor such that the exhaust results

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with a lot of soot and NOx formed. The presence of high EC and OC can be seen with sample V04 and V03 in figure 1 suggestive of a poisoned exhaust catalyst. Only sample V04 contained chloride ions, since the sector is a copper commodity therefore interference with the samples cannot be ruled out and the above result could be due to the strong bonds between the metal chromates and chlorides which the nitric acid could not dissolve.

Table 4 below illustrates the comparisons between the components detected in the samples.

DPM RESULTS (mg)										
	V01	V02	V03	V04	V05	V06	V07	V08	V09	V10
TC	0.05	0.09	**1.24**	**5.59**	**1.47**	**0.48**	**0.22**	**0.13**	**0.54**	**1.17**
EC	0.01	0.01	**0.89**	**4.93**	**1.26**	**0.24**	0.09	0.05	**0.39**	**0.72**
OC	0.04	0.08	**0.35**	**0.66**	**0.21**	**0.24**	**0.13**	0.09	**0.16**	**0.45**
TRACE ELEMENTAL DETERMINATION RESULTS (ppm)										
Al	**0.12**	**0.64**	**0.14**	**0.38**	**0.10**	**0.10**	**0.12**	0.05	0.03	0.06
Ca	**0.60**	**1.14**	**0.63**	**0.86**	**0.54**	**0.67**	**0.59**	**0.38**	**0.31**	0.05
Cr	0.01	0.02	0.00	0.01	0.00	0.00	0.00	0.00	0.00	**5.72**
Cu	0.03	0.02	0.01	**1.07**	0.00	0.00	0.00	0.00	0.00	**0.12**
Fe	**0.39**	**0.79**	**0.12**	**1.13**	**0.18**	**0.20**	**0.26**	**0.18**	0.06	**9.68**
K	**0.15**	**0.24**	**0.20**	**0.86**	**0.10**	**0.13**	**0.17**	**0.11**	0.04	-0.18
Mg	**0.27**	**0.39**	**0.11**	**0.24**	0.09	0.09	**0.14**	0.07	0.05	**0.11**
Na	**0.26**	**0.42**	**0.30**	**0.33**	**0.16**	**0.23**	**0.27**	**0.18**	**0.20**	0.05
Ni	0.07	0.03	0.02	0.04	0.02	0.02	0.01	0.01	0.02	**16.85**
V	0.00	-0.01	0.00	0.00	0.00	0.00	0.01	0.01	0.00	**0.15**
Zn	**0.14**	**0.20**	**0.23**	**0.26**	**0.04**	**0.25**	**0.09**	**0.14**	0.05	0.00
ANIONIC DETERMINATIONS RESULTS (ppm)										
Fluoride	0.01	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	**0.06**
O-phospha	-0.01	0.01	0.01	**0.05**	-0.02	0.00	-0.01	-0.01	-0.01	0.00
Sulphate	0.00	-0.13	**0.27**	-0.13	-0.13	-0.04	-0.05	**0.05**	-1.02	-0.35
Chloride	-0.65	-0.74	-0.67	**0.52**	-0.60	-0.87	-0.55	-0.59	-0.78	-0.69

Table 4: Comparisons of the effect of compositions contained by the samples

Table 4 indicates the presence of metals such Al, Ca, Cu, Fe, K, Mg and Na. Sample V04 showed to contain high amounts of Ca, Cu, Fe and K which could be an indication of the contribution by engine-oil and wear of the engine metals though the presence of Cu could highly be attributed to the abundance of copper from this mining sector. Relating all the results of sample V04 from figure 1, figure 5 and table 4, the presence of the phosphates, trace metals and high DPM (EC/OC) content could be an indication of wear and tear in the engine combustion chamber such that the engine oil reaches the chamber and burns along with the diesel fuel. The absence of sulphates for this sample indicates the purity levels of the diesel fuel used. Similar remarks can be made about sample V03

except that the all the results of this sample suggest a contribution of the impurities to be from the diesel fuel than any wear and tear. The presence of the high sulphate content in this sample relates to the amount of soot in the exhaust and is indicated by the DPM (EC/OC) content of the sample.

Based on all the results presented, samples V05 and V06 indicate the presence of wear and tear at a very low level in the engines; this is without ruling out the presence of impurities in the diesel fuel used even though no sulphate was detected. This assumption is suggested by the significant amounts of the trace elemental substances detected in the two samples and the high content of DPM (EC/OC).

Sample V10 also contained significant amounts of DPM (EC/OC) and trace elemental substances but the metals present seem to be as a result of the combustion of their abundance from the chrome mining sector without ruling out the presence of heavy diesel fuel though no sulphates were detected. This is suggested by the presence of the high chromium (Cr), nickel (Ni) and iron (Fe) contents even though the impurities in the diesel fuel and engine wear may not be ruled out. No other correlation from the given results exists for the remainder of the samples.

4   CONCLUSION

The presence of high elemental and organic carbon in some of the samples mentioned previously, V03, V05, V06 and V10 are an indication of an incomplete combustion of the diesel fuel in the engines combustion chambers. This could be due to a variety of reasons including the poising of the catalyst in the exhaust lines leading to a build-up of NOx and clogging, the leakage of engine oil into the engine combustion chamber and the impurities in the diesel fuel used. To identify the source of this high EC/OC content, the results of the trace elemental substances gave suggestions such as wear and tear from the engine components indicated by the presence of the combusted substances such zinc (Zn), magnesium (Mg), potassium (K), calcium (Ca) and aluminium (Al).The other suggestion was the presence of diesel fuel impurities indicated by the presence of vanadium (V), nickel (Ni), iron (Fe) and chromium (Cr).

 Further analysis for anions gave a clear indication in distinguishing if whether the OC/EC and trace elemental substances observed were due to tear and wear of the engine metals or due to diesel fuel impurities. The sought correlation between the three types of analysis (DPM analysis, trace elemental analysis and anions analysis) undertaken to obtain the results under discussion in this paper seem to be an important tool for identifying the source of diesel exhaust soot.

However, the method used to digest the DPM samples and analyse them for anions has a high limitation in terms of determining anions that are known to react with the digestion solvents used.

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