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Determination of Pollutants from Heavy Fuel Oil (HFO) Combustion in Power Plants

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تعيين المُلوثات الناتجة من حرقِ زيت الوقود الثقيل في محطات توليد الطاقة الكهربائية

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تتراكم مخلفات كربونية غير كاملة الإحتراق في قاع وعلى جدران مداخن محطات توليد الطاقة الكهربائية التي يستعمل فيها زيت الوقود الثقيل مصدراً للطاقة الحرارية. تتطلب هذه التراكمات الكربونية الإزالة الدورية لها وقد وجد أن هذه التراكمات ذات حموضة عالية تصل إلى 32.8% وزناً. كما أنها تحتوي مركبات أروماتية متعددة الحلقات المتكاثفة تصل إلى 707 جزء بالمليون.

عند دراسة حالة معزولة لمدخنة إرتفاعها 60 متراً لإحدى المولدات التي تستهلك 17.7 طناً كحد أعلى من الوقود الثقيل وتنتج 65 مليون واط في الساعة الواحدة فقد أظهرت هذه الدراسة تكوّن ما يلي ضمن غازات الإحتراق التي تطلق إلى الجو بواسطة المدخنة.

115.7±15.4 ملغم/م^3 من غاز ثالث أكسيد الكبريت (معدل ست قياسات ومجمع في 80% محلول مائي للكحول الآيزوبروبيلي) و317.5±91.3 ملغم/م^3 من غاز ثاني أكسيد الكبريت (معدل ثلاث قياسات ومجمع في 0.3% محلول مائي لبيروكسيد الهيدروجين) و88.2±75.2 ملغم/م^3 من غاز أول أوكسيد النيتروجين (معدل ثلاث قياسات ومجمع في محلول مائي يحوي 0.1 عياري من حامض الكبريتيك و0.3% بيروكسيد الهيدروجين).

جمعت الغازات أعلاه في نظام مصمم لهذا الغرض من منطقة محددة في جسم المدخنة وسحبت غازات الإحتراق بسرعة 2 لتر في الدقيقة وكانت كمية الوقود الثقيل المحروقة آنئذ تعادل 10.5م^3 بالساعة وكمية الهواء التي تم ضخها إلى الحارقة تعادل 140 ألف م^3 في الساعة.

جرى تعيين تراكيز المعادن الثقيلة في التراكمات الكربونية وفي الطابوق الناري المُبطن لجدار الحارقة وفي الوقود الثقيل قبل الإحتراق وحصلنا على النتائج المبينة أدناه للمعادن المختارة مقاسة بجزء بالمليون وهي على التوالي: الكروم (2.5±271.7، 15.4±386.9، <0.05)، المنغنيز (51.1±853.6، 39.0±544.9، <0.06)، النيكل (567.1±9278.3، 7.9±69.4، 1.7±3.18)، الزنك (2.0±327، 4.9±182.5، 0.1±0.73)، الفناديوم (1916.5±7956.1، 43.1±189.3، 0.8±1.45)، والحديد % (28.0، 0.92، <0.04).

وقد تم تعيين معادن ثقيلة أخرى هي الكادميوم والنحاس والرصاص وجرى تعيين جميع المعادن المذكورة بواسطة تقنية الإمتصاص الذري. ونظراً لخطورة تواجد المركبات الأروماتية متعددة الحلقة في نواتج الإحتراق فقد جرى إستخلاصها بواسطة المذيب ثنائي كلوريد الميثان من التراكمات الكربونية وتمت دراستها وتقدير تركيزها بواسطة كروماتوغرافيا الغاز الشعرية.

Abstract: *Carbon deposits highly contaminated by acids (32.8 wt. % on H_2SO_4 basis), and poly nuclear aromatics (PNA's; 707 ppm) accumulate and need periodical removal from a power station chimney. Heavy fuel oil (HFO) is used as the main fuel.*

SO_3 (115.7±15.4 mg/m^3), SO_2(317.5±91.3 mg/m^3), and NO (88.2±75.2 mg/m^3), in flue gas were determined. HFO consumption was 10.5 m^3.h^{-1} and air flow rate in the burner was140x10^3 m^3.h^{-1}.

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Heavy metals (ppm) Cr: 271.7±2.5, 386.9±15.4 and <0.05; Mn: 853.6±51.1 544.9±39.0 and <0.06; Ni: 9278.3±567.1, 69.4±7.9 and 3.18±1.7; Zn: 327±2.0, 182.5±4.9 and 0.73±0.1; V: 7956.1±1916.5, 189.3±43.1 and 1.45±0.80; Fe(%): 28, 0.92, and <0.04, in carbon deposits, fire-brick linings and HFO, respectively, were determined by atomic absorption spectroscopy. Other heavy metals, namely Cd, Cu and Pb were also determined. Polynuclear aromatics PNA's in CH_2Cl_2 extracts from carbon deposits were estimated by capillary gas chromatography.

INTRODUCTION

Among several orthopogenical activities, combustion of fuels in stationary plants is a major contributor to pollution by some combustion products such as sulfur oxides (SOx), nitrogen oxides (NOx) and particulate matter[1,2,3]. Of most concern, is the combustion of residual fossil fuels, such as heavy fuel oil (HFO).

Another aspect of increasing worldwide attention related to combustion of HFO is the fate of uncombusted and / or reformed organics released into the environment. It is well established now that the combustion of crude oil residues and heavy distillates results in a wide variety of organic pollutants which enter the environment in the form of gas, liquid and solid wastes[4,5]. Among these pollutants, polynuclear aromatic hydrocarbons (PAH; also called: polycyclic nuclear aromatics PNA), make up a class of concern due to their carcinogenic, teratogenic, mutagenic, and chronic low-level hazardous potential that may affect lower and higher organisms.

Heavy fuel oil is used as the main fuel in the Western Tripoli Power Station. The present paper gives the results of a study carried out on deposits in, and emissions from one of five small chimneys (60 m height) in the power station. There are two more bigger chimneys (120 m height). Accordingly, we carried out investigations covering the following aspects:

- Determination of heavy metal contents in the ash of carbon deposits, parent HFO, and in fire-brick lining of chimney.
- Estimation of SOx and NOx release as a result of HFO combustion.
- Studies on water and organic solvents extracts from carbon deposits in the chimney.
- Estimation of uncombusted hydrocarbon release with attempted elucidation of chemical structures of some of the released compounds.

EXPERIMENTAL

Experimental Procedures:

1- Separation of Uncombusted Organic Matter from Carbon Deposits in the Chimney:

Organics were separated using Soxhlet extraction system with toluene or dichloromethane solvents. 50 g (accurately weighed to four decimals) of dried (105°C for 2 h) carbon deposits (bottom; BCD or wall; WCD) were placed in a clean, dried, accurately weighed porcelain thimble, which was then placed in the Soxhlet extractor. 300 ml of solvent was added in the round bottom flask collector, and extraction was continued until no coloured extracts were observed (~12 h). Extraction was stopped, the thimble dried and the extracts were distilled in a rotary evaporator using a mild vacuum. Extracts were accurately weighed .

2- Estimation of Total Uncombusted Hydrocarbons in Flue Gases

Uncombusted hydrocarbons were separated from combustion gases using cooled solvent traps. Two solvents were used in the separation (one at a time), toluene and dichloromethane.

The trapping assembly consisted of:

- Stainless steel tube (180 cm x 0.4 cm internal diameter) to get the gas sample at least one meter deep in the main flow of stack.
- Solvent (aq. NaOH 1.0 N) traps
- Silica gel trap to protect the vac. pump.
- Vacuum pump equipped with gas flow meter and was adjusted to a flow of 1.5 l. $min.^{-1}$

When everything was set, the stopcock was opened, the pump was turned on, and the gas sample was drawn up to 500 liter total volume. At this point, operation was stopped,the solvent was distilled under mild vac. using a rotary evaporator, and the uncombusted organics were accurately weighed. Refer to Figure-1 for a diagram of the operation.

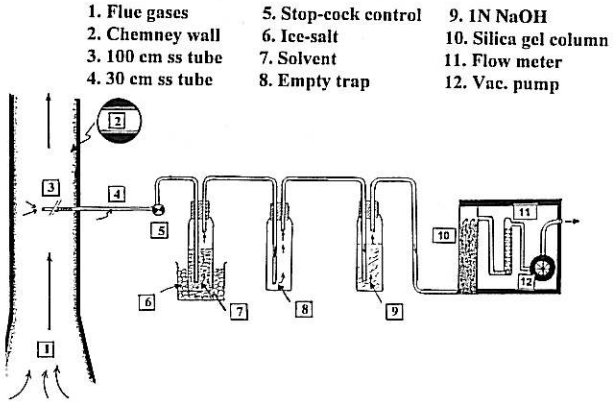


Fig. 1. Flue gas trap for uncombusted organics.

3- *Determination of Total Acidity of Flue Gases:*

A similar trapping system to that used in (2) above was used to determine the total acid content of flue gases. Two traps were used, the first one contained 500 ml, 2 N NaOH aqueous solution and the second one (between the first and the pump) was empty. The flow rate was adjusted to 1.5 l/min. and the operation was stopped after 500 liters were drawn. The amount of trapped acids was determined from the back titration of the NaOH solution. Acids were determined on a H_2SO_4 basis.

4- *Determination of Total Acidity of Water Extracts from Carbon Deposits:*

100 g of carbon deposits (B.C.D and W.C.D, one at a time) were refluxed (1 h) with 500 ml of distilled water. The mixture was then filtered and the deposits were washed several times with distilled water. The filtrate and the washings were combined and the volume was made up to 1 liter in a volumetric flask. The pH of the previous solution was measured. Samples of 50 ml of this solution were titrated against a standard 0.2 N NaOH solution using phenolphthalein as indicator. The total acid content was determined on a H_2SO_4 basis.

5- *Determination of Sulfate Ion in the Aqueous Extracts:*

The method used was that of **ASTM-D516**[6].

6- *Determination of Iron Content in the Aqueous Extracts from Carbon Deposits:*

The method used was that of **ASTM-C114**[7], which is basically used for the analysis of hydraulic cement .

7- *Determination of Ash Contents:*

The methods used were those of **ASTM-D482-(87)**,or **ASTM-D3174-(79)**[8] depending on the sample, whether liquid or solid.

8- *Determination of Heavy Metal Contents in Carbon Deposits:*

The method used with carbon deposits was that of **ASTM-D3683**[9].

9- *Determination of Heavy Metal Contents in Heavy Fuel Oil:*

A suitable weight of sample (10 g) was ashed into a platinum dish at 500°C in a muffle furnace with 0.5 g of p-toluenesulfonic acid. When ashing was completed (~30 min.), the residue was warmed gently with 10 ml of nitric acid (25%), stirring and crushing the ash with a glass or PTFE rod. The slurry was transferred to a 50 ml calibrated flask, washed with a further 10 ml of nitric acid (25 %) and 5 ml of cesium chloride solution (1 %) and diluted to the mark.

Calibration solutions were prepared from a stock standard and they contained the same concentrations of nitric acid and cesium chloride as the sample solutions.

10- *Separation and Determination of Individual Polluting Gases: SO3 SO2 and NO.*[1]

(a) Collection and Determination of SO_3:

200 liters of flue gases, withdrawn from the chimney at a rate of 4 l. min^{-1}. were passed through a liquid trap of 80% iso propyl alcohol in distilled water (400 ml IPA + 100 ml H_2O). The gases were kept warm by wrapping the stainless steel connecting tube with asbestos tape, since SO_3 dew point is about 44°C. At the end of the experiment, SO_3 content in the trap was determined by titration against 0.01 N NaOH aqueous solution using phenolphthalein as an indication.

(b) Collection and Determination of Total SO_2+NO

Gases leaving the SO_3 trap in (a) above, were split by a three-way stop cock and were passed simultaneously at a rate of about 2 l. min^{-1}. into two liquid traps; one for total SO_2 + NO and the other for NO alone.

The total SO_2 +NO stream was allowed to pass through 500 ml of 0.3 % H_2O_2 aqueous solution. At the end of experiment, SO_2 + NO content (after being oxidized to SO_3 + NO_2 by H_2O_2) was determined by titration against 0.01 N NaOH aqueous solution using phenolphthalein as an indicator. The SO_2 content in flue gas was deduced by subtracting the corresponding value related to NO which is determined in (c) below.

(c) Collection and Determination of NO:

The split stream of stack gases from (b) above was passed through 500 ml of 0.1 N H_2SO_4 in 0.3% H_2O_2 aqueous solution. A diagrammatic representation of the operations is given in Figure-2. At the end of the experiment, the solution was made alkaline with 1 N KOH and was evaporated to dryness; gently without any spattering (about 24 h).

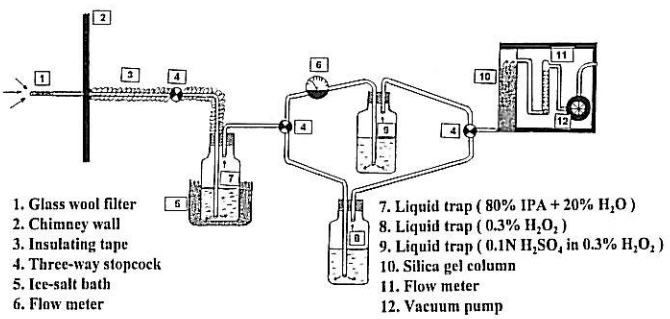


Fig. 2. Liquid trap for SO_3, SO_2 and NO.

10 ml of phenoldisulfonic acid reagent (PDS) "see *d* below" was added to the residue from evaporation, the solution was shaken and was transferred quantitatively, to a 100 ml volumetric flask, using distilled water. Visible light absorption in the range 400-430 nm was obtained (the solution may be diluted if necessary). The concentration of NO_2 was determined from a calibration curve of concentration Vs absorption intensity in the range 400-430 nm of KNO3 standard solutions containing known amounts of PDS reagent in both samples and reference cells.

(d) Preparation of PDS Reagent:

It is prepared as follows:

Phenol	25 g
Conc. H2SO4	150 ml
15% Oleum	75 ml

11- Gas Chromatographic Experimental Conditions for the Determination of Poly-Nuclear Aromatics (PNA):

The chromatographic conditions employed by us in the separation of PNA's are listed in (A) below. Meanwhile, the GC-Conditions employed by the American Environmental Protection Agency [EPA] for the separation of the 16 standard PNA's[125], are listed in (B). The variation in conditions, as given in the two sets (A and B), may afford an explanation for the small differences in the retention times of some of the expected PNA's compared with the standard ones.

Chemicals and Instruments:

- Chemicals used were of analytical grade obtained from Aldrich, UK.
- GC carried out using PACKARD 439.
- Heavy metal determined using AAS/A. A-1475,
- Sulfur determined using ANALIR, Analyzer instrument.
- GC 312 pumps used to withdraw gases from chimney
- pH meter used was KNICK DIGITAL-pH-METER 646

A	B
PRC- GC- Col . Conditions	**EPA - 610 / GC- Col. Conditions**
Column: 25m x 0.25mm (L x ID) WCOT CP-Sil CB (df = 0.12μm)	Column: 25m x 0.25mm (L x ID) Ultimetal WCOT CP-Sil PAH CB (df = 0.12μm)
Temperature: 35°C - 280°C rate 5°C/ min.$^{-1}$	Temperature: 70 C - 300 C / min-1.
Carrier gas: N_2, 60 KPa (0.6 bar,); 25ml/min^{-1}.	Carrier gas: H2, 100 KPa (1.0 bar, 15 psi); 30 cm/s
Injector: spliter, 100 ml / min^{-1}. (T = 300°C)	Injector: spliter, 100 ml / min-1. (T= 325°C)
Detector: FID, 1 x 10 -11AFS (T = 300°C)	Detector: FID, 2^3 (T= 350°C)
Sample size: 1.0μl	Sample size: 0.5μl

- Muffle furnace LINN. HIGH THERM VMK22 used for ashing.

RESULTS AND DISCUSSION

The *Western Tripoli Power Station*, first established in 1976, is situated on the Mediterranean shore, about 20 km west of Tripoli center. Heavy fuel oil (HFO) is used as the energy source for steam generation. The station is composed of two power plants, the descriptions of each are given in Table 1.

There also exists a desalination plant and treatment units. The power station is surrounded by farms and village residential communities from all directions except the north side. Prevailing wind is from north to south in most seasons, thus, farms and populations are exposed to pollution from emissions from this power station.

Figure -3 gives an illustrating diagram for the boiler, gas flow, sampling location and definition of carbon deposits (bottom carbon deposits, B.C.D and wall carbon deposits W.C.D with respect to chimney).

Table 1. Western Tripoli Power Station.

Property	Plant A	Plant B
- No. of generators	5	2
- Capacity; mega watt.h^{-1}	5x65	2x120
- Stack height; meters	60	120
- Amount of HFO consumed, Tons.h-1 at max. loading	17.7	28.5

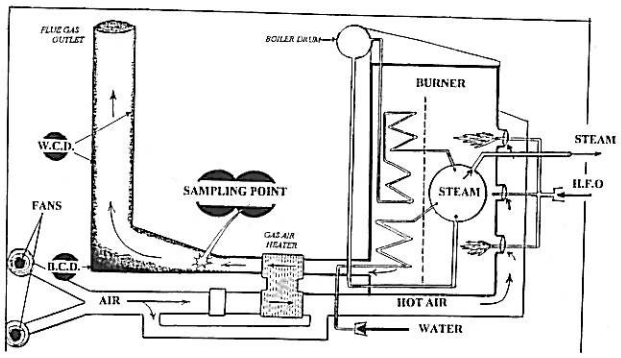


Fig. 3. Boiler air and gas flow.

Temperatures in the burner and boiler zones are also indicated.

Sampling and operation conditions with other information of interest are given in Table-2. It is obvious that our results and conclusions represent only a small portion of operations taking place at the power station. All our investigations were carried out on one of the five small chimneys in plant A (Table-1), defined as Unit 2.

In our investigations, we focused first on the carbon deposits (C D) in the chimney. A pile of over 50 cm deep of these deposits was noticed on the chimney's floor (B.C.D), and about 15 cm thick deposits on the inside walls (W.C.D). It is well established that incomplete combustion of fossil fuels produces carbon deposits, along with a variety of reformed and/or partially oxidized hydrocarbons. It is also expected that carbon deposits will be contaminated with inorganic acids as a result of the production of acid gases during combustion.

Extraction of CD with CH_2Cl_2 in a soxhlet system produced a higher hydrocarbon content, but less combustibles in WCD (Table-3). The results in this table further indicate a very high iron content in the ash of CD (especially in BCD). This prompted us to carry out full analysis on heavy metals content in BCD, WCD the fire brick lining of the chimney's interior, and ash in the parent HFO. The results are given in Table-4. Fire brick (FB) is also used to line the interior of the burner. The results in Table-4 indicate that FB may be the source of the relatively high contents of Fe, Mn, Pb, Cr, Zn, and Cu in the carbon deposits. On the other hand, the HFO is a considerable precursor of Ni and V.

The water extracts from carbon deposits was found to be highly acidic. This is to be expected given the type of fuel used (HFO) and the combustion conditions. The results on pH and amount of acid in CD on the basis of H_2SO_4 equivalence, are given in Table-5 .

Table 2. Sampling and operation condition*

Sampling conditions			Operation conditions			
Sample No.	Sample type	Sampling date	Air flow (m3h)	Fuel (ton/h)	Power (mega watt)	Stack temp. (°C)
1	Hc.	19.1.95	170	13	40	135
2	Hc.	19.1.95	170	13	40	140
3	T.acid	26.1.95	160	15.5	42	140
4	T.acid	26.1.95	145	12.5	40	135
5	Hc.	30.1.95	160	13	42	135
6	Hc.	30.1.95	160	13	42	135

* As designed.
- Sampling location : Unit 2.
- Sampling duration : 4 h.
- Flow rate (l.min^{-1}): 2
- Sample vol. (l): 500.
- Combustion temp. C°: 1370.
- Hc: hydrocarbons.
- T. acid: Total acids.

Table 3. Bottom & wall carbon deposits analysis

Sample	% Ash	% Iron	% Organics (% hydrocarbons)	% Combustables (and/or decomposebles)
B C D	47.67	28	0.11	52.33
W C D	66.5	4.6	0.43	33.5

Table 4. Average concentration(X) of heavy metals(1)

Element	B C D (ppm)	W C D (ppm)	F B (ppm)	H F O (ppm)
Cd	59.54±4.3	27.7±3.1	7.1±0.46	< 0.06
Cr	271.7±2.5	49.7±2.8	386.9±15.4	< 0.05
Cu	173.9±11.3	47.2±2.1	38.0±2.9	< 0.04
Fe %	28.0(2)	4.6(2)	0.9(2)	< 0.04
Pb	4161.2±11.5	259.5±10.4	51.7±1.5	< 0.34±0.6
Mn	853.6±51.1	1828.9±70.8	544.9±39.0	< 0.06
Ni	9278.3±567.1	92.3±18.4	69.4±7.9	3.18±1.7
Zn	327±2.0	74.7±6.1	182.5±4.5	0.73±0.1
V	7956.1±1916.5	1825.8±147.2	189.3±43.1	1.45±0.8

(1) Average of three determinations.
(2) By gravimetric & Titrimetric Analysis.A single determination was conducted

Table 5. Acids in bottom & wall carbon deposits

Sample	PH	N* (g.ml^{-1})	Total acid (H_2SO_4 basis) (g/l)	% Acid in deposits (H_2SO_4 basis)	SO_4=** (ppm)
B C D	1.5	0.015	16.4	32.8	11145
W C D	1.6	0.008	9.8	19.6	5390

* N Grams of NaOH needed for neutralization of acids
** Determined gravimetrically

It is well established that sulfur in fossil fuels converts mainly to SO_2 on combustion of fuel[2,3].

$$\underset{\text{fossil fuel}}{C, H, S, ...} + O_2 \longrightarrow \underset{99\text{-}98\%}{SO_2} + \underset{1\text{-}2\%}{SO_3} + CO_2 + H_2O + \text{etc.} \quad (1)$$

It is also well documented in literature, that active conversion of SO_2 to SO_3 is catalyzed by Fe and Mn oxides present in the fly ash of the same heavy fuel employed[3].

$$SO_2 + {}^1/_2O2 \xrightarrow{Fe/Mn} SO_3 \quad (2)$$

$$SO_3 + H_2O \longrightarrow H_2SO_4 \quad (3)$$

Fe and Mn salts are also present in the composition of fire bricks lining the interior of the burner and chimney (refer to Table-4) and may play an important role in this conversion (Equation-2) through surface catalysis. This may

also account for continuous abrasion of the lining and accumulation with the carbon deposits. To further supplement and justify the choice of H_2SO_4 equivalence for the estimation of total acid content in CD, a gravimetric determination of sulfate ion content in the aqueous extracts from CD was performed. The results are given in Table-5. BCD contained more than twice the amount of sulfate ions than WCD.

Separation of the principle polluting gases: SO_3, SO_2 and NO individually from flue gas, using liquid traps as shown in Figure-2, made reliable assessment of the contribution of each gas possible. The choice of the specified liquid traps is based on previous work[1]. Thus, the determination of SO_3 in flue gas is based on the work of Alyea and Backstrom[10] who found that several higher alcohols inhibited the oxidation of dissolved SO_2. Flint[11] selected isopropanol (IPA) because it is miscible with water, its inhibiting action extended over long periods of time, and the solubility of SO_2 in IPA solutions was considerably lower than in distilled water. Absorption in 80 % IPA has been the most widely used collection method[11,12] for SO^3 in power plants.

Aqueous hydrogen peroxide absorbing solution has been widely used for the collection of SO_2[11,13], where:

$$SO_2(g) + H_2O \longrightarrow H_2SO_3\ (aq.) \xrightarrow{H_2O_2} H_2SO_4\ (aq.) \quad (4)$$

Collection of SO_2 in H_2O_2 is the technique required by EPA for checking compliance with new source performance standards (power plants etc.) under the Clean Air Act of 1970[15].

Nitric oxide (NO) is the only oxide of nitrogen present in significant concentrations at flue gas temperatures. It is mainly formed as a result of the reaction of O_2 and N_2 of the air at flue combustion temperatures. Thermodynamically, the oxide is unstable and dissociates back to its elements at all temperatures:

$$^1/_2\ N_2 + {}^1/_2\ O_2 \rightleftharpoons NO \quad (5)$$

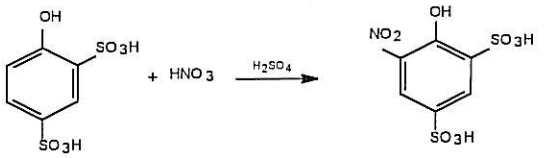
Phenoldisulfonic acid (PDS) is the most widely used reagent for NO_x determination in flue gases and it has been adopted as a standard method by EPA[13,14] and other standards[16]. Beatty, *et. al.*[17] used 0.1N H_2SO_4 in 0.1% H_2O_2 as the absorbing solution and recently up to 0.4% H_2O_2 has been used. The peroxide serves a two-fold purpose, namely to oxidize any nitrate and to convert sulfite, an interference, to sulfate i.e.:

$$NO + H_2O_2 \longrightarrow NO_2 + H_2O \longrightarrow HNO_3 \quad (6)$$

$$SO_2 + H_2O_2 \longrightarrow SO_3 + H_2O \longrightarrow H_2SO_4 \quad (7)$$

H_2SO_4 does not interfere with the quantitative color production which will be explained below.

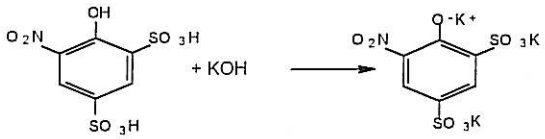
After absorption, the solution is made alkaline with potassium or sodium hydroxide and slowly evaporated to dryness to avoid spattering losses. PDS is then added to the dry solid residue and a nitration reaction takes place:



(8)

Phenol-2,4-disulfonic acid (PDS) | Phenol-6-nitro-2,4-disulfonic acid (PNDS) | (Formed in solution)

The yellow colour produced on making the solution alkaline is due to the ionization of the phenolic proton from the 6-nitrophenol-2,4-disulfonate:



(9)

PNDS | Yellow

The yellow color produced is measured between 400 and 430 nm with a spectrophotometer. The color intensity is related to concentration and assessed quantitatively from a calibration curve.

The results obtained for determining SO_3, SO_2 and NO concentration in milligrams per cubic meter (mg/m3) of flue gas, are given in Table-6 (a and b). It is obvious from these results that considerable conversion of SO_2 to SO_3 does take place under the combustion conditions. It is well established that only 1 to 2 percent of SO_3 is

usually produced on burning in air of sulfur containing fossil fuels such as HFO. The average results on SO_3 content in Run No.'s 1,2 and 6 in Table - 6a, and those in Run No.'s 1,2 and 5 in Table - 6b, on SO_2 content, indicate that SO_3 concentration (in mg/m^3) is about 28% that of the total SO_x produced during the combustion of HFO containing 0.5% sulfur. This strongly points that a considerable catalysis is taking place. Such catalytic effect is probably occurring through the action of Fe and Mn oxides in the ash and/or through the action of other metals present in the composition of the fire-brick lining in the burner and chimney walls.

Table 6a. Concentration of SO3[1] in flue gas from the combustion of HFO[2][3] in Western Tripoli Power Station

Run No.	Vol. of 0.01N NaOH needed (ml)	Total NaOH consumed (g/m^3)	H_2SO_4 equivalence (mg/m^3)	SO_3 equivalence (mg/m^3)	Date of run
1	2.6	0.130	159.3	130.1	30.1.96
2	2.3	0.115	140.9	114.6	30.1.96
3	2.0	0.100	122.5	100.0	6.2.96
4	2.6	0.130	159.3	130.1	6.2.96
5	1.9	0.095	116.4	94.6	6.2.96
6	2.5	0.125	153.1	124.5	6.2.96

(1): Collected in 80%IPA aqueous solution .
(2): HFO consumption 10.5 $m3.h^{-1}$ and air flow rate in the burner $140x10^3$ $m^3.h^{-1}$
(3): HFO sulfur content is 0.5% .
- Sample collection flow rate 2 $l.min^{-1}$, vol. of gas collected = 200L
- Liquid trap volume = 500 ml.
- Titrated portion volume = 20 ml.

Noticeable concentration of NO is also produced as a result of the operating conditions in this power plant. An average value of 88.2 mg/m^3 NO is produced in the Run No.'s 1,2 and 5 (Table - 6b) compared to 317.5±91.3 mg/m^3 (Table 6b) and 115.7±15.4 mg/m^3 (Table 6a), for SO_2 and SO_3 respectively. This comparison further indicates that about 17% of the total (SO_x + NO_x) emission is in the form of nitrogen oxide (NO) expressed in mg/m^3. Chemical conversions in the manner outlined earlier (equations 1, 2, 3 and 5) might take place producing the observed SO_x and NO_x distribution.

We thought it is necessary to put some emphasis on uncombusted and/or reformed organics released into the environment during the combustion of fossil fuels. By far, the main anthropogenic source of PNA's is incomplete combustion of fossil fuels.

Up to date, the power of the combined capillary column GC/MS system is the top analytical technique for the separation, estimation and identification of individual PNA's[18-23]. In our laboratory, we tried to throw some light on PNA's in CD using capillary column GC only.

In a recent publication[24], emphasis on dichloromethane (CH_2C_{12}) as a model PNA solvent was registered, therefore, we used CH_2Cl_2 to extract (soxhelt), and to trap organics from CD and flue gases respectively. The results on total amount of organics trapped were 998 ppm, 4280

Table 6b. Concentration of SO_2[1] and NO[2] in flue gas from the combustion of HFO[3] in Western Tripoli Power Station

Run No.	Vol. of 0.01N NaOH needed (ml)	Total NaOH consumed (g/m^3)	Portion of NaOH reacting with HNO_3 (mg/m^3)	Portion of NaOH reacting with H_2SO_4 (mg/m^3)	SO_2 equivalence (mg/m^3)	NO equivalence (mg/m^3)	Date of run
1	3.6	0.36	69.1	290.9	231.6	51.8	30.1.96
2	6.2	0.62	233.1	386.9	307.6	174.8	30.1.96
3	3.2	0.32	-	-	-	-	6.2.96
4	3.8	0.38	-	-	-	-	6.2.96
5	5.7	0.57	50.6	519.4	413.4	38.0	6.2.96

(1): Collected in 0.3% H_2O_2 aqueous solution, then determined by titration againest NaOH.
(2): Collected in 0.1N H_2SO_4 in 0.3% H_2O_2 aqueous solution, then determined spectrophotometriclly using PDS method .
(3): HFO consumption 10.5 $m^3.h^{-1}$ and air flow rate in the burner $140x10^3$ $m^3.h^{-1}$.
- Sample collection flow rate 2 $l.min^{-1}$, vol. of gas collected = 100L
- Liquid trap volume = 500 ml.
- Titrated portion volume = 20 ml.

ppm and 0.0848 g/m^3 for BCD, WCD and flue gases respectively.

In order to throw light on the nature of the CH_2Cl_2 extracted organics from CD, detailed capillary column gas chromatographic investigation was carried out on three extracted samples from each of BCD and WCD. The specification of the GC column, the running conditions and results are given in Table-7 for BCD and in Table-8 for WCD. Although running conditions are not exactly matched with those given in literature[25] on the conventional sixteen PNA's proposed by the American Environmental Protection Agency [Project EPA - 610], tentative comparisons of our results and relevant observations and conclusions may be drawn. A major conclusion is that several PNA's are present in the CH_2Cl_2 extracts from

Table - 7 GC of CH_2Cl_2 extract from bottom carbon deposits (B C D)

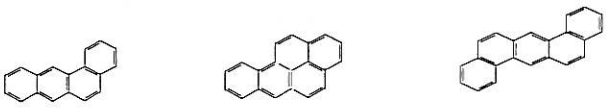
B C D_1		B C D_2		B C D_3		EPA[25]	
R.T.O (min)	CONC. (ppm)	R.T.O (min)	CONC. (ppm)	R.T.O (min)	CONC. (ppm)	Name formula	R.T.S (min)
-	-	-	-	-	-	Naphthalene $C_{10}H_8$	4.24
10.5	40.6	10.2	11.1			Acenaphthylene $C_{12}H_8$	10.65
-	-	-	-	11.4	11.00	Acenaphthene $C_{12}H_{10}$	11.8
-	-	-	-	-	-	Fluorene $C_{13}H_{10}$	15.16
-	-	-	-	-	-	Phenanthrene $C_{14}H_{10}$	21.28
23.8	44.00	-	-	-	-	Anthracene $C_{14}H_{10}$	21.64
-	-	-	-	-	-	Fluoranthene $C_{16}H_{10}$	29.94
-	-	-	-	-	-	Pyrene $C_{16}H_{10}$	31.36
40.4	364.7	40.1	402.8	39.9	322.0	Benz[a]anthracene $C_{18}H_{12}$	40.51
40.7	32.0	40.4	37.5	42.5	31.5	Chrysene $C_{18}H_{12}$	40.80
47.8	5.7	47.5	61.5	46.9	26.00	Benzo[b]fluoranthene $C_{20}H_{12}$	48.08
49.3	29.1	48.6	18.4	-	-	Benzo[k]fluoranthene $C_{20}H_{12}$	48.31
51.0	64.00	49.00	75.9	51.7	15.5	Benzo[a]pyrene $C_{20}H_{12}$	49.85
56.0	28.2	55.6	20.3	55.3	28.7	Benzo[ghi]perylene $C_{22}H_{12}$	56.72
-	-	57.6	157.0	57.6	101.0	Indeno[1,2,3-cd]pyrene $C_{22}H_{12}$	57.38
58.0	8.6	58.1	18.3	-	-	Dibenz[ah]anthracene $C_{22}H_{14}$	58.00
Total GC detected PNA (ppm)	616.7		968.4		535.7		
Total Hc content (ppm)	906		1183		906		

R.T.O = Retention time / observed.
R.T.S = Retention time / standard.

BCD and WCD, but we cannot assign accurately any specific retention time to a certain PNA member. An observation worth mentioning from Tables 3, 7 and 8 revealed the amount of organics in WCD is about four folds higher than that in BCD. This suggests that the higher we go up in the chimney the higher the concentration of expected PNA's. In other words, a noticeable release of PNA's occurs as a result of burning HFO as a source of energy at the *Western Tripoli Power Station.*

In Table 9 (a and b), the structures of some strong carcinogenic PNA's and the percent of total area measured by GC of related carbon numbers, are listed.

Table 10
(a) Structure of some carcinogenic PNA's



Benzo[a]anthracene ($C_{18}H_{12}$) Benzo[a]pyrene ($C_{20}H_{12}$) Di-Benzo[ah]anthracene ($C_{22}H_{14}$)

(b) Percent of total area measured by GC

Cx	BCD_1	BCD_2	BCD_3	average BCD	WCD_1	WCD_2	average WCD
C_{18}	44	48.6			13.7	17.3	15.5
(40.51)	(40.4)	(40.1)	(39.9)		(40.1)	(41.5)	
C_{20}	10.7	13.2	4.6	9.3	3.0	3.9	3.5
(49.85)	(51.0)	(49.0)	(51.7)		(50.8)	(46.9)	
C_{22}	10.3	16.6	14.3	13.7	2.4	5.1	3.8
(58.0)	(58.0)	(58.1)	(57.6)		(56.9)	(56.9)	

*Values in brackets represent retention times in mints.

CONCLUSIONS AND RECOMMENDATIONS

In a very broad sense, two major conclusions may be drawn from this study:

1- Flue gases form the combustion of heavy fuel oil (HFO) in *Western Tripoli Power Station* and the amount of fuel combusted daily may pose health hazards to people, animals, and plants and cause property damage under certain meteorological conditions; when air is stagnant. However, in order to give fair assessment of the effects of pollutants; SOx, NOx, Particulate, PNA's etc. it is imperative to conduct seasonal monitoring at specified distances from the station in all directions (except North), taking meteorological conditions into consideration.

2- Highly acidic, extremely enriched heavy metals and PNA's containing carbon deposits, which are removed periodically from the chimneys, pose serious dangers no matter where these deposits are disposed of; on land or in the sea. We recommend the following scheme to deal with these deposits.

i- Adjusting the combustion operation conditions, or injecting steam to reduce the carbon deposits formation to minimum.

ii- When the above is not attainable, the deposits may be washed with a dilute base (*e.g.* 0.01 N NaOH) to neutralize the acidity.
The acid free deposits may be used as a solid fuel, after mixing with a petroleum pitch, or be used as a filler in road paving.

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