

PAH CHARACTERISTICS IN SEDIMENT AROUND

by Muhammad Syahrir

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PAH CHARACTERISTICS IN SEDIMENT AROUND MAKASSAR COAST USING GC-FID

¹⁾ Muhammad Syahrir ²⁾ Nurul Hidayat Aprilita ³⁾ Nuryono ⁴⁾ Netti Herawati

^{1) 4)} Department of Chemistry, FMIPA UNM

^{2) 3)} Department Chemistry, FMIPA UGM

e-mail: syahrir_gassa@yahoo.com or m.syahrir7406@unm.ac.id

Abstract. Waste parameter characteristics in 17 sediment sampling stations around Makassar Coast are salinity, turbidity, pH, and temperature and it can be concluded that the highest turbidity is at station 14, it is 50.3 NTU while the lowest content is at station 3, it is 0.67 NTU. Measurement of the highest pH concentrations is at station 10 location, it is 8.21, while the lowest is at station 9 location, it is 7.62. Temperature measurement does not show its maximum results according to signals of Ministerial Environmental Preservation Decree number 112 of the year 2003. The highest salinity at its station 6, it is 37 per mile, and the lowest salinity is at station 14, located on a river in power plant surrounding area, with its normal requirement is 33-34 per mile. Collected sediment samples are taken to the laboratory in order to be analyzed their PAH with sample preparation using dichloromethane solvent and organic extracts obtained are fractionated using Silica-gel chromatography column – Alumina and GC-FID instrument. Evaluation of GC-FID separation is done by determining its capacity, selectivity, recovery, and repeatability factors. The research result shows its capacity, selectivity, and repeatability factors are sufficient enough. In validation methods, linearity parameters, linear range, limit of detection (LOD) and limit of quantification (LOQ) for each PAH provide a linear regression coefficient (r) close to 1 and limit quantifying (LOQ) is three times greater than limit of detection (LOD). Total PAH concentration in its sediments of all stations majority obtained in Station 1, Station 5, Station 6, station 9, station 10 and station 15 respectively (740.78; 1121.4; 1140.07; 960.62; 852, 22 and 633.25) ppm. Station 5 and station 6 are shopping complex and dense traffic. Then station 9 is close to large population activity and Tallo River estuary as well as Makassar industrial area and landfill waste in Antang. If it is compared with Ministerial Environmental Preservation Regulation, the three stations PAH levels are found in its sediments already exceed the threshold where its minimum requirement is 0,003 ppm for Biota and greater than 200 ppm for sediment.

Keywords: Characteristics, stations, Method Validation, Concentration, PAH

INTRODUCTION

Indonesia consists of 17,508 islands with a length of coastline is more than 81,000 kms and 70% of its population live in its coastal region (Nontji, 1997 & 1999). This situation is very favorable considering the enormous potential of sea, both as a source of abundant natural and as a means of transportation, trade and tourism. Countries bordering on Malacca Strait has been successfully agreed on the terms in addressing environmental issues, but law enforcement efforts on handling of environmental issues in that Straits has not been implemented due to both inter-agency coordination in law enforcement has not been integrated (Suhaidi, 2005).

Lukitaningsih (1999) compares two PAH analysis methods in sediments by HPLC and GC-FID. Obtained results, its selectivity and accuracy degrees are higher by GC-FID compared with HPLC with reference to an EPA (Environmental Protection Agency) standard procedure. Sample preparation using *soxhlet* extraction has many

weaknesses in them, possibility of an emulsion, many of its number of organic solvents are used, resulting in an organic solvent waste in large quantities, the extraction process takes a long time, and cannot be done automatically. This method is convenient enough for analysts because they do not have too much interaction directly with chemicals used and tools are generally available in all Chemical Laboratory in Indonesia, making it possible to analyze accurately when a neighborhood indicated the existence of PAH. Research related to this as well as a variety of methods have been developed e.g EPA 610, EPA 8270 C methods, Golledge, WR, & Herzfelder, ER (2004, 2009), in preparation of sediment samples prior to extraction generally uses wet sediment without drying which takes 1 x 24 hours to keep under 4° C condition is transferred from its environment to the laboratory and stored in *freeze dried* or refrigerator. Viewed from its shortcomings of this method, it would require an appropriate method to modify EPA 610, EPA 8270 C method, Golledge, WR, & Herzfelder, ER (2004, 2009).

This method modification uses dry sediment samples at room temperature and a small sample thus simplifying in analysis. Based on this description it is interested for researchers to conduct research with development of standard operating procedures title in PAH analysis around Makassar Coast.

RESEARCH METHODS

Sediment Sampling

Dry sediment sampling at room temperature on sediment surface of around Makassar Coast is at the same time with sample categorization.

The number of samples is taken around 30 grams per one blank sample. Distance and depth of sampling is varied (2-5 m) depending on whether the sample muddy or sandy condition. The surface temperature of the water at the site is measured using a pH meter. The degree of acidity (pH) of each station is measured using a pH meter.

Sampling technique

Pre-sampling phase

Sample handling from field to laboratory is performed in 3 phases. The first phase is to clean all tools before sampling. At tool cleaning stage, glassware such as 2 L glass bottles are soaked and washed with soapy water and then they are rinsed with distilled water. Afterwards, they are oven-dried at a 100 ° C temperature.

Sampling phase

Sediment samples are taken at sea or river waters. All samples are taken at the same time. Sediment samples are taken during rainy season or dry season using a *Van Veen grab*, and then they are stored in a boxer taken in the coast location surrounding.

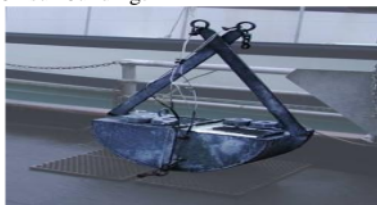


Figure 1 Van Veen Grab tool used in sampling sediments (Golledge&Herzfelder, 2004)

During dry sediment sampling, room temperature is sterilized so that no contamination from other sources of unwanted contaminants comes. The sediment samples taken with that device is inserted into a plastic and wrapped

with aluminum foil in order to prevent from outside petroleum contamination and they are taken to the laboratory and then they are dried at room temperature.

Post-sampling phase

At this stage, deposit sediment samples are directly dried in laboratory at room- temperature. Unfiltered sea water is stored in *gerry* at 30-35°C room temperature and characterization sea water turbidity and water content measurement is conducted.

RESEARCH MATERIALS AND TOOLS

Research Materials

PAH Standard is obtained from Aldrich (Darmstadt) including: Naphtalene, Pyrene, Fluorantene, Phenanthrene, Acenaphtene, Perylene, Benzo(a)pyrene. Other chemicals: anhydrous sulphatenatrium, 70-240 mesh silica gel, alumina, quality p.a fabricated by E.Merck, while helium gas, hydrogen, and nitrogen are fabricated by Aneka Gas. In addition to those materials also used n-hexanesolvent, dichloromethane that has quality p.a fabricated by E.Merck. Water used is *aquabides* of Pharmaceutical Lab. and distilled water produced by LPPT UGM, FMIPA UNM Chemistry Lab. and Instruments Analytical Chemical Lab. of Ujung Pandang Engineering Chemistry Polytechnic.

Research tools

Tools used in this research are glass tools, soxhlet (Pyrex), Liebiq cooler (Pyrex), heating mantle (CE), a beaker (Pyrex), measuring glass (Pyrex), flask (Pyrex), stir bar (Pyrex), desiccators (Pyrex), while pipette and distilled water bottle (Brand), a spatula (Indonesia), magnetic stirrer (CMSI), a mortar and pestle (China). Tools used for evaporation are *Buchii R II rotary evaporator*, vacuum pump (*Hitachi, Ltd.*), number 18 1:00 mm sieve (*Fisher Scientific Company*), Al.204 analytical balance (*Mettler Toledo*), 501 model oven (*Fisher*). Tools used on the field are a thermometer (100 °C) of *Hanna HI 8314*, *refractometer* hand, Van Veen Grab, 76 CSX Garmin type GPS (*Global Positioning System*), gas tubes from Aneka Gas, turbidimeter, color bottles and rope, micropipette (Gilson), blender (*Waring*), injector (*Hamilton Co.*), Vortex (*Maxi Mix II*), *Eppendorf, blue tip*, and a *yellow tip*, are tools used to analyze extracted samples with FID detector gas chromatography of QP 2010 Shimadzu.

PAH ANALYSIS

Standard solution preparation

PAH standard solution is made by weighing ± 0.01 grams per PAH (Naphthalene, Acenaphtene, Fluorantene, Phenanthrene, Pyrene, Benzo(a)anthracene and Perylene) with following steps: (a) 0.01 grams of PAH standard compound is added to 10 ml volumetric flask to make a 1000 ppm solution. (b) PAH standard compound is dissolved with DCM (<10 ml) in 10 ml flask and added DCM into it right up to its mark to make 1000 ppm solution stock. (c) 500, 100, 20, 10, 5, 2, 1, and 0.5 ppm standard solution is prepared by diluting process.

VALIDATION METHOD

Linearity and linear range determination

Calibration curve Preparation

Calibration curve describes response of an instrument to a measured value. In this case, the pertinent value is analyte concentration (PAH solution standard), while its instrument responses are in the form of absorbance of GC-FID tools. Regression line and regression coefficient (r), a (intercept) and b (slope) can be obtained based on statistical calculations of the respective PAH curve.

$$Y = a + bx$$

Based on that calculation, each value will be obtained. These quantities are used to calculate limit of detection (LOD) and limit of quantification (LOQ) as described in the following section.

Determination of the limit of detection (LOD) and the limit of quantification (LOQ)

Limit of detection (LOD) is the lowest analyte concentration that can be detected reliably by a method and it is statistically different to signals originate from a blank through a complete treatment method, including chemical extraction or initial sample preparation. Limit of Quantification (LOQ) is the lowest analyte concentration that can be determined quantitatively with acceptable accuracy and precision when the method is applied (SNI 19-17025-2000 quoted from ISO 17025: Suheryanto, 2010). Mathematically $LOD = Yb + 3 Sb$ and $LOQ = Yb + 10 Sb$.

Information:

Yb = equation intercept regression

Sb = standard deviation slope

5.4. Precision determination by test

Repeatability

The repeatability is conducted by a test with 10 blank samples with standard compound under same conditions, same analyst, same tools and laboratory and testing time is almost simultaneously with stages as follows:

1) 10 pieces of blank are prepared 2). Test is done by validation/verification of all 10 sample blank methods. 3) In measurement process, each sample is measured twice and its average is calculated between samples (X) and its deviation standard (SD) 5) Relative standard deviation (RSD) is calculated using the formula:

$$RSD = (SD/X) \times 100\%$$

Acceptance of RSD value to repeatability is as follows (Table 1):

Table 1. Analyte concentration to maximum

Analyte Concentration	Maximum Horwitz% RSD
100%	2
10%	2.8
1%	4
0.1%	5.7
100 ppm	8
10 ppm	11.3
1 ppm	16
100 ppb	22.6
10 ppb	32
1 ppb	45.3

(Horwitz, 1995)

Sediment sample extraction

10 grams of sifted dried sediment sample is put into a 250 ml round bottom containing dichloromethane and n-hexane (50-50 = V/V) of each 100 ml. 1 ml-seven standard compound each 10 ppm (naphthalene, acenaphthene, fluorantene, phenanthrene, pyrene, benzo(a)anthracene, and perilena) is added to a 250 ml round bottom flask in section 4.3.1 above. Soxhlet extracts sample for 18 hours, then it is cooled to room temperature. Solvent is extracted and filtered and solvent is evaporated by Buchii Evaporator at a 45° C temperature. Sample is removed, filtered and dried with sodium sulfate or glass wool and then put into a small bottle and left until its temperature becomes cold (Organic Materials Extraction/EBO). PAH fraction is separated from the aliphatic hydrocarbon fraction by cleaning-up and fractionation of aromatic fractions is analyzed its GC-FID.

FRACTIONATION

Fractionation sediment samples

Aliphatic and aromatic fractions (PAH) are separated from EBO by using chromatography columns. The adsorbent used is 70-240 mesh silica gel and alumina (1:1 = v/v). Fractionation columns to be used are cleaned from other hydrocarbons and its bottom is coated with *glass wool* or cotton to keep the idle and not qualified phase during elution is in progress. With *slurry* technique, 1 cm of Na₂SO₄ anhydrous, 7 grams of silica gel, 7 grams of alumina and 1cm of Na₂SO₄ anhydrous and enough filter paper successively inserted into the fractionation column. That column is filled with n-hexane to its brim and eluted repeatedly.

Silica gel and alumina are made into *slurry* with eluent to be used and then put into columns a little while its column faucet is opened. Fractionating columns are eluted continuously with normal hexane to homogeneous alumina-silica gel. Silica-gel top (surface) is covered with filter paper to hold that sample. EBO obtained from that sample extraction is weighed and then it is dissolved in 1 ml of n-hexane and poured into the column and subsequently it is eluted with 20 ml of normal hexane to obtain aliphatic fraction. In order to get aromatic fraction/PAH column is eluted with 20 ml of DCM : n-hexane (1:1). Separation of aliphatic and PAH fraction is helped by UV light, PAH fraction will look fluorescent, while aliphatic will not. After that solvent is evaporated, each fraction is then weighed carefully by an analytical balance to determine the weight. Then its aromatic fraction is dissolved in 1000 ml of DCM solvent and analyzed by GC-FID.

Samples sediment Analysis by GC-FID

All prepared sample validation methods are analyzed by Ujung Pandang Polytechnic GC-FID to perform accurate search method.

Aromatic fraction containing PAH is analyzed by GC-FID with Rtx-5 column. 7 standard compounds individually or in mixtures (naphthalene, acenaphthene, fluorantene, phenanthrene, pyrene, benzo (a) anthracene, and perilena are in that *sample*. PAH Fraction is injected into GC.

GC experimental condition used by using RTX-5 column type is a column length of 30.0 m, 0.32 mm ID column diameter, 330° C maximum temperature column, oven temperature: initial temperature of 60.0° C and the hold time 1,00 min, time of 36.5 minutes, the rate of 8° C/min with a temperature of 290.0° C and the hold time of 6.75 minutes, FID detector type with temperature condition detector of 315° C, carrier gas He 2-3 ml/minute, carrier gas flow rate of 400 mL/min, H₂ flow rate of 35 mL/minute as well as air make-up of 30.0 mL/minute.

PAH concentration calculation

PAH analysis is conducted by extracting sediment sample soxhlet, green shellfish and aromatic fractions containing PAH is analyzed by gas chromatography and quantified its PAH concentration.

RESEARCH RESULT

Parameter Characteristics of Waste

From those four parameters measured, those are, salinity, turbidity, pH, and temperature, it can be concluded that the highest turbidity is at station 14 (power plant), it is 50.3 NTU while the lowest content is at station 3 (Recreation/Akkarena), it is 0.67 NTU. From the height of parameter turbidity at station 14 (power plant), it is assumed that happens because at station 14, there are very various activities such as disposal of food remains from restaurant, disposal of a final waste facility at Antang, oil from garages, waste from power plant and intensity waste disposal by surrounding population is higher and increases. Based on the turbidity concentration according to Ministerial Environmental Preservation Decree number 112 of the year 2003 related with waste water quality standards for biota, then turbidity on station 14 location indicates high pollution levels. Signal recommended by the Ministerial Environmental Preservation Decree is 5 NTU, while pH signaled parameters recommended in Ministry of Environmental Preservation number 112 of the year 2003 on the quality of waste water quality standards for biota is 7 to 8.5.

While the results obtained from the 17 observation station points shows that the highest concentration of pH is at station 10 location (Port), it is 8.21. While the lowest is at station 9 location (Port), it is 7.62. From the lowest to the highest range of pH concentrations at a number of station locations are at normal pH condition by the Ministerial Environmental Preservation Decree of the year 2004. The temperature parameters at 17 sampling stations show station 8 and station 16. This shows because that area is a residential area with its main activity fishing while at station 16 in the surrounding area is near Sukarno-Hatta harbor and other domestic waste disposal for example fish auctions and other activities. While temperature parameter at 17 sampling station locations does not show its maximum results in accordance with signal of Ministerial Environmental Preservation Decree number 112 of the year 2004. Details can be seen in Table 1.

Important aspects in determining of sea water density are temperature, salinity, and pressure. Density will go down if the temperature rises and bigger if the pressure and salinity increases. Usually, if the temperature is lower and then its density will increase. Besides that, the increase in salinity can also increase value of seawater mass density, although it is not as strong as temperature effect (Thamrin Marsaoly, 2010).

The highest salinity is at station 6, it is 37 per mil, while the lowest salinity is at station 14 located on a river in area near power plant, with its normal requirement is 33-34 per mil. Based on salinity measurement results show maximal and it is not in accordance with signal of Ministerial Environmental Preservation Decree number 112 of the year 2003. Details can be seen in Table 1.

Validation Methods

Validation method used is to use several parameters: 1) Linearity 2) Limit detection (LOD) and Limit 3) quantification (LOQ) 4) Accuracy 5) Range Linear. PAH targets are analyzed by GC-FID QP-2010 all PAH targets can be identified by retention time and peak height produced higher (Figure 1).

Based on the chromatogram, a mixture of PAH standard targets are identified by retention time of each PAH (Naphthalene; Acenaphthene; Phenanthrene; Fluorantene; Pyrene; Benzo (a) anthracene; Perylene) are (10.755; 16.318; 21.023; 24.911; 26.631; 29.553; 35.364) seconds.

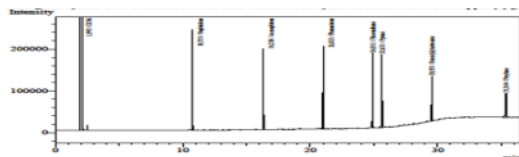


Figure 1. Mixed standard PAH chromatogram of 1000 ppm by GC-FID QP-2010 (Syahrir, 2013).

Table 2. Characteristic of each sediment sampling station at around Makassar Coast.

Station	1	2	3	4	5	6	7	8
Station Activity	River estuary	River	Play Ground	Old Jeneberang R.	Shop	Residence	Residence/Bridge	Residence
Depth (m)	4	2,5	2,5	4	3	3	3	4
Salinity (o/oo)	31	25	30	35	35	37	12	32
Turbidity (NTU)	41,5	6,12	0,67	4,08	1,39	0,8	3,57	0,99
pH	8,07	7,98	8,14	8,18	8,13	8,17	7,7	8,18
Temperature (oC)	30	29	30	30	30	30	29	31
Coordinate	05° 11,605 SL 119° 22,741 NL	05° 11,634 119° 23,199	05° 10,085 119° 23,124	05° 12,144 119° 22,920	05° 09,023 119° 23,745	05° 09,007 119° 23,994	05° 09,108 119° 24,363	05° 08,217 119° 23,622
Station	9	10	11	12	13	14	15	16
Station Activity	Port	Port	Estuary	Estuary	Upper course	Upper course	Power Plant	Industrial Area
Depth (m)	2	4	4	4	5	3	3	4
Salinity (o/oo)	30	33	33	30	10	0	20	35
Turbidity (NTU)	1,73	2,3	2,2	1,85	3,41	50,3	2,73	3,1
pH	7,62	8,21	8,24	8,19	7,64	7,76	7,84	8,02
Temperature (oC)	29	30	30	30	30	28	30	31
SL Coordinate	05° 06,559 119° 25,202	05° 06,088 119° 25,726	05° 05,714 119° 26,385	05° 05,510 119° 26,526	05° 06,638 119° 26,490	05° 08,715 119° 28,404	05° 05,165 119° 26,586	05° 03,544 119° 27,922
Station								17
Station Activity								Pier
Depth (m)								3
Salinity (o/oo)								34
Turbidity (NTU)								18,8
pH								8,06
Temperature (oC)								30
SL Coordinate								05° 03,650 119° 28,022

Evaluation of Separation:

Proceedings of *ICMSTEA 2016* : International Conference on Mathematics, Science, Technology, Education, and their Applications, Makassar, Indonesia, 3rd – 4th October 2016

Retention factor (capacity = k'):

Qualify k' value requirement is more than 1 (one) except in Naphtalena.

Capacity factor is calculated with this formula:

$$k' = \frac{tr - tm}{tm}$$

in which, tr is the retention time of PAH target, and tm is retention time of mobile phase. The capacity factor (k'):
Determination of Capacity Factor tr is retention time of PAH tm is retention time of mobile phase

1	PAH type	tr (min)	tm (min)	Capacity Factor (k')
	Naphtalene	10.76	1.99	4.39
	Acenaphtene	16,32	1.99	7.19
	Phenantrene	21.02	1.99	9.55
	Fluoranthene	24.91	1.99	11.5
	Pyrene	25.63	1.99	11.86
	Benzo(a)anthracene	29.55	1.99	13.83
	Perylene	35,36	1.99	16.74

Qualified between $1 < \alpha < 10$ (Harold M. Miller M. Mc. Nair & James, 1997). The relative separation between two adjacent peaks is described by selectivity or separation factor (α), which is defined as the ratio of the capacity factor of two peaks:

$$\alpha = \frac{k_2'}{k_1'} = \frac{tr_2 - tm}{tr_1 - tm}$$

If the price is above 1 means α relative separation between two adjacent peaks PAH pretty good. Selectivity factors - Factors Determining Selectivity

From result of selectivity factor determination above, it shows selectivity value is greater than 1. This qualifies as a condition of selectivity of a separation between two adjacent peaks is quite good, except on *naphtalene* compounds.

Type PAH	tr (min)	Separation of PAH	Selectivity Factors
1			
Naphtalene	10.76	Naphtalene and Acenaphtene	0
Acenaphtene	16.32	Acenaphtene and Phenantrene	1.64
Phenantrene	21.02	Phenantrene and Fluorantene	1.33
Fluoranthene	24.91	Fluorantene and Pyrene	1.20
Pyrene	25.63	Pyrene and benzo (a) anthracene	1.03
Benzo(a)anthracene	29.55	Benzo(a)anthracene and Perylene	1.17
Perylene	35,36	Perylene	1.21

Number of Theoretical Plates

Qualify N_{req} over 7000 so that the expected frequency of occurrence of the equilibrium of the analyte in the stationary phase and a mobile phase can enable the achievement of the separation of PAH is formed (Grob., 1995). By using the following formula:

$$\begin{aligned} \text{Number of theoretical plates } (N_{\text{req}}) &= 16 \left(\frac{16,318}{0,205} \right)^2 \text{ for Acenaphthene compound} = 101378,6 \\ \text{Number of theoretical plates } (N_{\text{req}}) &= 16 \left(\frac{21,023}{0,215} \right)^2 \text{ for Phenanthrene compound} = 152979,2 \\ \text{Number of theoretical plates } (N_{\text{req}}) &= 16 \left(\frac{24,911}{0,088} \right)^2 \text{ for Fluoranthene compound} = 1282144 \\ \text{Number of theoretical plates } (N_{\text{req}}) &= 16 \left(\frac{25,631}{0,229} \right)^2 \text{ for Pyrene compound} = 200438 \\ \text{Number of theoretical plates } (N_{\text{req}}) &= 16 \left(\frac{21,023}{0,233} \right)^2 \text{ for Benzo (a)anthracene compound} = 257401,6 \\ \text{Number of theoretical plates } (N_{\text{req}}) &= 16 \left(\frac{35,364}{0,308} \right)^2 \text{ for Perylene compound} = 210931,4 \end{aligned}$$

The number of theoretical plates (N_{req}) = u ntuk compound *perylene* = 210,931.4

From all PAH types above the N_{req} are qualified, that is more than 7000 so that the expected occurrence frequency of analyte equilibrium in stationary phase and a mobile phase can enable PAH separation achievement is perfectly formed (Grob., 1995).

From these data (Table 2) above for N_{req} against GC-FID using RTX-5 column has value of theoretical plate *Naphtalene* = 44038,56, *Acenaphthene* = 101378,6, *Phenanthrene* = 152979,2, *Fluoranthene* = 1282144, *Pyrene* = 200438, *Benzo(a)anthracene* = 257401,6, and *perylene* = 210,931.4, where the number plates of all target theoretical PAH is qualified at more than 7000 except on perylene, where the number plates of all target theoretical PAH is qualified at more than 7000 so that the expected occurrence frequency of analyte in the stationary equilibria phase and a mobile phase can enable PAH separation achievement is perfectly formed (Grob., 1995).

Table 2. Capacity Factor and Number of Theoretical Plates of each PAH target from GC-FID CP Sil 8 CB column analysis results

type PAH	tr (min)	Number of theoretical plates (N_{req})	capacity factor
<i>Naphtalene</i>	10.7 6	44038.56	4, 40
<i>Acenaphthene</i>	16.3 2	101,378.6	7.19
<i>Phenanthrene</i>	21.0 2	152,979.2	9.55
<i>Fluoranthene</i>	24.91	1282144	11,50
<i>Pyrene</i>	25.63	200 438	11.86
<i>Benzo (a)Anthracene</i>	29.55	257,401.6	13.83
<i>Perylene</i>	35,36	210,931.4	16.74

t_r is PAH retention time
 t_m is retention time of 1.993 minutes at mobile phase

Table 3. The average retention time of each standard PAH in GC analysis FID using Rtx-5 column

PAH	Retention time 1	Retention time 2	Retention time 3
	(minutes)	(minutes)	(minutes)
<i>Naphtalene</i>	10.80	10.79	10.79
<i>Acenaphthene</i>	16.35	16.34	16.35
<i>Phenanthrene</i>	21.03	21.03	21.03
<i>Fluoranthene</i>	24.90	24.90	24.90
<i>Pyrene</i>	25.65	25.65	25.65
<i>Benzo (a)Anthracene</i>	29.59	29.58	29.59
<i>Perylene</i>	35.44	35.41	35.42

5
The limit of quantification (LOQ) and the limit of detection (LOD)

Table 4. Value of LOD, LOQ, linear range, R, and PAH Standard Calibration Curve Equation

PAH Target	LOD (ppm)	LOQ (ppm)	Rentang.Linear (ppm)	Rate R	Calibration curve equation
1 <i>Naphtalene</i>	0.80	3.9 3	0-50 & 50-1000	0.994 0.996	$y = 551.4x + 807.9$ $y = 571.4x + 7099,$
<i>Acenaphtene</i>	0, 70	2.32	0-50 & 50-1000	0.986 0.997	$y = 492.9x + 2217,$ $y = 507.2x + 7463,$
<i>Phenantrene</i>	0.84	2.8 2	0-50 & 50-1000	0.992 0.998	$y = 544.8x + 1549$ $y = 571.6x + 4561,$
<i>Fluoranthene</i>	0.7 5	2, 50	0-50 & 50-1000	0.989 0.998	$y = 500.3x + 2000$ $y = 545.4x + 4028,$
<i>Pyrene</i>	1.13	3.7 8	0-50 & 50-1000	0.989 0.999	$y = 510.1x + 1862$ $y = 556.9x + 3281$
<i>Benzo (a) anthracene</i>	0.9 6	3, 20	0-50 & 50-1000	0.997 0.999	$y = 344.7x + 969.1$ $y = 342.8x + 2824,$
<i>Perylene</i>	0.80	3.9 3	0-50 & 50-1000	0.991 0.998	$y = 374.9x + 603.0$ $y = 306.9x + 8049,$

Table 4 shows that LOD value below that concentration has not been detected while LOQ value is 3 times greater than LOD. In addition it is also supported by the highest R value of 0.997 in *benzo (a)anthracene* compound 0.986 and the lowest in *Acenaphtene* compound, generally close to value 1.

THE PRECISION (TEST RECOVERY)

This method accuracy is determined by addition standard method and it is expressed as recovery percent (recovery). Recovery determination is conducted by adding 20 microliters of PAH standard with a concentration of 1 ppm, 2 ppm and 4 ppm for blank sediment sample.

Recovery test method above (Table 5) shows that sediment samples using adduct standard methods (additional standard into sample) can still be found after it is being analyzed by GC-FID with the highest score 132% on a compound *benzo (a)Anthracene* and the lowest is at *Acenaphtene* compound, it is 49.6343 %, while other compounds are in range of 80-120 % (AOAC, 2002) as required means that this method has good accuracy test.

Table 5. Recovery value list the on addition of PAH standard 1, 2 and 4 ppm against A blank sample of sediment at Lae-lae Island

PAH Target	1 ppm	SD	2 ppm	SD	4	SD	Average	SD
<i>Naphtalene</i>	31.58	3.43	33.78	5.43	5.22	0.32	23.52	3.72
<i>Acenaphtene</i>	22.71	11.19	80.19	11.19	75.88	16.96	59.59	13.11
<i>Phenantrene</i>	55.69	0	68.49	0	66.53	41.55	63.57	13.85
<i>Fluoranthene</i>	92.41	34	128.40	34	110.30	55.06	110.4	41.02
<i>Pyrene</i>	45.07	6.68	110.8	6.68	135.60	68.49	97.16	27.28
<i>Benzo (a) Anthracene</i>	125.8	45.50	89.31	59.66	114.80	68.97	110	58.04
<i>Perylene</i>	0	0.832	95.64	22.94	81.20	38.78	88.42	20.85

Based on Table 6 above shows that total PAH concentration of each station obtained at stations 5, station 6, and station 9 (1121.4, 1140.07 and 960.62) ppm.

While station 5 is a shopping complex and station 6 is Makassar Transtudio complex

and dense traffic. Then station 9 is close to a large population activity and near the end of Tallo river as well as the existence of PT Galangan Kapal, Makassar Industrial area and Final Disposal landfill in Antang where its waste sits at Tallo river.

CONCLUSION

Based on test validation methods that use several parameters including:

1. Linearity, linear range, LOD, LOQ, and accuracy show that method used has been validated properly.
2. The most PAH concentration of each station obtained is in station 5, station 6, and station 9 (1121.4, 1140.07 and 960.62) ppm. Where station 5 is a shopping complex and station 6 is
3. Makassar Transtudio complex and dense traffic. Then station 9 is close to large population activity and near the end of Tallo river as well as their PT Shipyard and Makassar Industrial area and Final Disposal landfill in Antang
4. Where its waste sits at Tallo river. When compared with the station's third MKLH Regulation PAH levels were found in sediments already exceed the threshold where the minimum requirement is 0,003 ppm to 200 ppm for biota and sediment.

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Table 6. PAH Concentration in sediment sample at around Makassar Coast in ppm

PAH Target	1	2	3	4	5	6
Naphthalene	2.02 ± 0.17	6.08 ± 2.56	Nd	nd	Nd	Nd
Acenaphthene	Nd	Nd	Nd	1.36±1.09	Nd	Nd
Fluoranthene	Nd	5.26 ± 0.94	0.067 ± 0.95	17.58±2.19	1.929±1.929	1.093±1.544
Fluoranthene	Nd	Nd	Nd	nd	Nd	Nd
Pyrene	4.63 ± 4.63	Nd	228.36±5.59	nd	479.50±479.59	Nd
Benzo(a)Anthracen	Nd	149.70±211.71	15.72±4.96	10.62±15.02	388.18±496.734	933.23±3.81
Perylene	734.13 ± 1038.22	183.93±183.93	150.29±19.76	411.73±9.81	251.70±154.97	205.75±19.2
PAH Total	740.78	345.02	394.437	441.31	1121.4	1140.07
PAH Target	9	10	11	12	13	14
Naphthalene	Nd	nd	2.62±3.70	7.08±0.79	Nd	Nd
Acenaphthene	26.58±37.58	Nd	Nd	Nd	Nd	Nd
Fluoranthene	Nd	Nd	9.94±8.39	6.51±0.71	1.20±1.70	4.15±0
Fluoranthene	4.96±7.01	Nd	Nd	Nd	Nd	Nd
Pyrene	42.33±46.88	479.59±678.25	Nd	Nd	Nd	Nd
Benzo(a)Anthracene	50.79±71.83	20.87±2.73	17.05±19.65	12.84±18.13	147.35±208.39	Nd
Perylene	298.14±378.59	85.96±73.29	297.07±416.49	292.21±29.94	98.93±43.26	202.041±0
PAH Total	78.79±20.12	852.22	326.68	318.64	247.48	206.19
	960.62					

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