Determination of iron content within iron sands from Lampanah-Lengah estuary using various analytical methods

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Abstract. Lampanah-Lengah iron sand deposit has been analysed by several researchers using XRD, and being reported that it contains hematite and magnetite. The accuracy of iron content data is crucial to analyse due to the economic benefit and environmental consequences. This current study aims to compare the accuracy of several analytical methods to convince the iron content finding. Several methods that were AAS, UV spectrophotometric, gravimetric and redox titration methods were calibrated by determining the iron content of pure iron powder (p.a. Merck) prior to analyse the iron content in Lampanah-Lengah iron sand sample. The accuracy of each method was 99.51; 99.26; 98.82; 96.41% respectively. However the iron contents found in Lampanah-Lengah iron sand sample was significantly different from various analytical methods. The finding were 60.49, 39.58, 34.82, 55.33 and 43.0 wt% detected by AAS, UV spectrophotometric, gravimetric and redox titration methods respectively. It concluded that AAS methods was recorded as the most accurate method for iron content determination in iron sand sample. The iron content is comparable to the common iron content in most samples of iron sand previously reported in several places in Indonesia.

1. Introduction
Iron sand deposit in Lampanah-Lengah village, District of Aceh Besar, Indonesia has attracted researchers and investors, but the environmentalist concerns the pollution effect on coral reef nearly if it is mined. The environmental risk refers to a previous study reported in US that iron induced black-coral death especially on P. meandrina coral [1]. Some also argue it will stimulate the economic growth in surrounding area [2]. Many researchers have conducted some studies in Lampanah Lengah; however the iron contents in the iron sand were analyzed with a single method and each gave different data. Their study was based on magnetic separation and followed by XRD analysis, the deposit was reported containing mainly magnetite, Fe3O4 [3]. Another report show it contained 81% of Fe2O3 based on precipitation methods [4]. The magnetite is from main rock in upstream and is eroded by river to downstream up to estuary [5]. Other group claimed it has 92% of iron content in form of hematite which was extracted by using carbon reduction to form pig iron. These findings are considered very high compared to iron content reported in other location in Indonesia such as Sulawesi, which is only 66.7-79.5% of FeO based XRD analysis method [6].

Since the iron content data in iron sand at this location was reported higher than the common natural ore, this study aims to compare several methods to analyzed iron content in similar source of
sample. The methods are employed in this study are XRF, AAS, UV spectrophotometric, gravimetric and redox titration [7]. The objective of this study is to search the real iron content in the iron sand Lampanah_lengah by using several methods and to confirm the method with iron standard so that each method shows the accuracy. This information is crucial to the local government for their consideration of the exploration and the cost of risk environmental consequences.

2. Material and Methods

2.1 Sampling location
Sample was collected from three stations at estuary of lampanah-lengah at several coordinates. Iron sand was sampled by using a tabular soil sampler. Sampling location was recorded by GPS, the first location with coordinates (05° 14'02" LU, 95° 07 '10" BT) or (05° 14 '02" U, 95° 07 '10" T). It was near the Krueng Lengah estuary, with a depth of one meter. The second point was taken at a distance of 300 meters at the Krueng Lengah estuary whose coordinates (05° 14 '34" LU, 95° 01' 21" BT) or (05° 14 '34" U, 95° 01 '21" T). The sample was taken at a depth of one meter. Furthermore, the third point was taken with a distance of 600 meters from Krueng Lengah which is located near the Krueng Deureuma estuary in Lampanah Village with coordinates (05° 15 '09" LU, 95° 34' 31" BT) or (05° 15 '09" U, 95° 34' 31" T). Each sample was washed with distilled water several times dried and mixed truly before send to analyses.

2.2 Chemical and instrument
Chemicals used in this study were iron sand, iron powder (99.5%, Merck), hydrochloric acid (HCl) (37%), potassium thiocyanate (KSCN, p.a, Merck), nitric acid (HNO₃, 65%, p.a, Merck), ammonia (NH₃, 99.9%, Merck), ammonium nitrate (NH₄NO₃, ACS, >98%), potassium permanganate (KMnO₄, Merck, 99.3%), sodium oxalate (Na₂C₂O₄, Merck, 99.8%), mercury (II) chloride (HgCl₂, Merck, 99%, 5%), tin (II) chloride dihydrate (SnCl₂.2H₂O, Merck, 98%), manganese sulphate tetrahydrate (MnSO₄.4H₂O, BDH, 98.5%), phosphoric acid (H₃PO₄, 85%, Merck), sulphuric acid (H₂SO₄, Merck, 95.5%), X-Ray fluorescence (XRF Bruker S2 Ranger), UV-Vis Spectrophotometric Spelco 2000 and AAS (AA-3600 Shimadzu) were used for sample analyses.

2.3 Sample preparation
Weighed exactly 10.000 grams of iron sand, dried in an oven with a temperature of 104°C-110°C until constant weight. The dried sample was weighed 1.0000 grams, grounded and dissolved with 6 mL concentrated HCl was added with a ratio of w / v (iron sand: HCl = 1: 6) at 80°C for 1 hour. Next, the filtrate is was diluted with distilled water up to 100 mL in volumetric flask [8].

Similar procedure was repeated by dissolving iron powder (Merck grade, 99.5%) with 6 mL concentrated HCl was added with a ratio of w / v (iron sand: HCl = 1: 6) at 80°C for 1 hour. The filtrate was diluted with distilled water up to 100 mL and marked as standard primer solution. Some text.

2.4 Spectrophotometric methods
The standard iron solution was pipetted 1 mL transferred in a 50 mL volumetric flask and 1.5 mL of 4 M HNO₃ was added to oxidize it into iron (III) and then 2.5 mL of 2 M KSCN was added. The mixture was diluted up to 50 mL. This procedure was repeated by adding various volume of iron (III) solution to prepared various concentration of sample iron (III) that were 2, 3, 4 and 5 ppm. The absorbance was recorded after 40 minutes (stabilization time), (pH 1) at 550 nm by using UV-Vis spectrophotometry methods. The calibration curve was plotted and adjusted the standard solution concentration until the absorbance in range of 0.2-0.8. Similar procedure was followed for iron sand sample solution by pipetting 0.1 mL of iron sand solution and diluted up to 100 mL. Three mL of 4 M HNO₃ was added and 5 mL 2M KSCN subsequently added. When the color change stable (40 minutes) then the absorbance was recorded [9].
2.5 Gravimetric methods
Fifty mL of standard iron (III) solutions was pipetted and then 2 mL of 4 M HNO₃ was added into solution to oxidize iron ion. The mixture was diluted up to 100 mL and heated until boil. Then 2-3 drops of the orange methyl indicator was added before drop wise addition of NH₄OH solution with mole ratio iron to hydroxide was 1: 2 until the the solution changed from red to yellow. After all residue has precipitated out (15-30 minutes), the precipitate was filtered and washed several time with distillated water [10] (Fischer, 1961). The precipitate including the filter paper were transferred into porcelain crucible and calinated at 800°C for 1 hour. The sample was cooled down and kept in desiccator and weight as Fe₂O₃.

2.6 Atomic Absorption Spectroscopy (AAS) methods
Standard iron solution was diluted to prepare several standard solutions with concentration of 0.5; 1; 1.5; 3; and 5 ppm. The absorbance was recorded by using AAS and the calibration curved was plotted accordingly. Similar method was followed for determination of iron in iron sand solution by pipetting 1 mL of the iron sand sample solution was diluted up to 100 mL solution.

2.7 Titration methods
Standard solution of KMnO₄ was standardized by using sodium oxalate. Sodium oxalate (0.5 g) was dried in oven at 110°C for 2 hours, then cooled down then exactly 0.2028 g was dissolved in 100 mL sulfuric acid that previously prepared (6 mL of concentrated sulfuric acid up to 108 mL distillated water). The solution was heated up near to the boiling point. The temperature titration was maintained 70°C. The solution was titrated with potassium permanganate that was previously prepared (dissolving 0.8250 grams of KMnO₄ in warm distillated water, diluted up to 250 mL). Reaching the end point, titration was carefully done drop wise with time interval of 30 seconds and stopped at the end point titration (light pink) [10]:

\[
mEq. \, KMnO_4 = \frac{mEq. \, Na_2C_2O_4 \times N \times mL}{mass \, ekivalen}
\]

Determination of iron content in iron sand; ten mile liter of iron sand solution stock solution was pipetted, then 2 drops of stannous chloride (dissolved 1.500 grams of SnCl₂.2H₂O in 10 mL of 6 M HCl) that freshly prepared were added. Subsequently, it was quickly added 1 mL of H₂Cl₂ (dissolved 5.00 grams of HgCl₂ in 100 mL of aquadest) with stirring till the mixture turned white. The mixture was diluted 30 mL of aquadest and added 2.5 mL of Zimmermann-Reinhardt reagent (7 grams of MnSO₄.4H₂O in 50 mL of aquadest, added by stirring 12.5 mL of concentrated sulfuric acid and 12.5 mL of phosphoric acid), the mixture was diluted to 100 mL (Fischer, 1961). The mixture then, was titrated with standardized potassium permanganate solution. The procedure was repeated to determinate the iron content in standard iron sample (pure iron powder).

\[
\% \, Fe = \frac{(N \, KMnO_4) \times (VKMnO_4) \times (eqiv \, mass \, Fe) \times 100}{sample \, (mg)}
\]

3. Results and Discussions
All samples from each station has no significant different in physical parameters that is pH (8.34; 8.30; 8.32), temperature (31.9; 32.0; 32.8), DO (mg/L; 4.5; 4.5; 4.5). The thickness of sediment in 100 m depth were at station I (27 cm), at station II (11 cm), and at station III (25 cm) as shown in Figure 1.
Figure 1. The sediment level in each station (a) station I, (b) station II, (c) station III

The pH wet iron sand at each station was pH 8 which is considered basic and this condition stimulate decompose the mineral into water [11]. The temperature of the sand on the beach is relatively normal [12].

3.1 Iron content determination by spectrophotometric method

In spectrophotometric methods, reaction between $[\text{Fe(H}_2\text{O)}_6]^{3+}$ with SCN$^{-}$ gave a stable complex ion of $[\text{FeSCN(H}_2\text{O)}_5]^{2+}$ as the reaction ;

$$[\text{Fe(H}_2\text{O)}_6]^{3+} + \text{SCN}^{-} \rightarrow [\text{FeSCN(H}_2\text{O)}_5]^{2+}$$

The absorbance was recorded stable after 40 minutes of reaction and remained stable at least up to 60 minutes. The absorbance is stable in high acidic medium at least up to pH 1, and it started decrease at higher pH.

The complex follows the Lambert Beer law as shown in the calibration curve Figure 2, the plot line is straight with $r^2 = 0.99$, intercept (c), the correction error very low which is 0.02. Since diameter of covet is 1 cm, then the molar extinction coefficient ($\varepsilon$) is 0.1406 ppm$^{-1}$ cm$^{-1}$.

Figure 2. (a) comparison color between cyanide complexes of iron standard & iron sand sample, (b) plot of calibration curve standard

The iron content in iron sand of Lampanah-Lengah was 39.58% which lower than iron sand in Bireuen, it was 42.887% and very closed to those from Suka Bumi Selatan that was 39.69% [13-14]. The iron content in pure iron powder was 99.2557%.
3.2 Iron content determination by XRF method

XRF analysis was carried out at Institute Technology Bandung using standard procedure analysis including chemical and mechanical sample treatment. The minerals content based on XRF data as shown in Table 1. It confirmed that the dominant component of hematite and not magnetite was found in the Lampanah-Lengah iron sand. Iron in form of Fe₂O₃ (hematite) was 43%wt, and Fe₂O₃ was 61.48%wt.

| Compounds | m/m% | Std Err | EI | m/m% | stdErr |
|-----------|------|---------|----|------|--------|
| Fe₂O₃     | 61.48| 0.25    | Fe | 43   | 0.17   |
| SiO₂      | 15.77| 0.18    | Si | 7.37 | 0.09   |
| TiO₂      | 6.53 | 0.12    | Ti | 3.92 | 0.07   |
| Al₂O₃     | 3.84 | 0.11    | Al | 2.03 | 0.06   |
| CaO       | 4.20 | 0.10    | Ca | 3.00 | 0.07   |
| MgO       | 3.84 | 0.10    | Mg | 2.31 | 0.06   |
| Na₂O      | 1.88 | 0.07    | Na | 1.39 | 0.05   |
| MnO       | 0.629| 0.03    | Mn | 0.487| 0.024  |
| V₂O₅      | 0.385| 0.019   | V  | 0.216| 0.011  |
| P₂O₅      | 0.322| 0.016   | Px | 0.141| 0.007  |
| K₂O       | 0.254| 0.013   | K  | 0.211| 0.011  |
| SO₃       | 0.204| 0.010   | Sx | 0.0816| 0.0041 |
| Cr₂O₃     | 0.108| 0.005   | Cr | 0.0740| 0.0037 |
| ZrO₂      | 0.0942| 0.0047 | Zr | 0.0697| 0.0035 |
| ZnO       | 0.0561| 0.0028 | Zn | 0.00451| 0.0023 |
| SrO       | 0.0134| 0.0009 | Sr | 0.0113| 0.0008 |

*Source: all data was copied from the XRF printed data*

3.3 Iron content determination by volumetric and gravimetric methods

Iron content was determined based redox indirect titration, where iron (III) ion reacted excess tin (II) following standardized methods in permanganometric [15]. KMnO₄ as the titrant was standardized by using sodium oxalate. End point titration was recognized by changing color of KMnO₄ from violet into light pink as shown in Figure 3(a). The iron sample was added excessive SnCl₂ as shown in this reaction:

\[
2\text{Fe}^{3+} + \text{Sn}^{2+} \rightarrow 2\text{Fe}^{2+} + \text{Sn}^{4+} \quad (3.1)
\]

The excess of Sn²⁺ reacted with Hg²⁺ and form a precipitate Hg₂Cl₂ and Sn⁴⁺:

\[
\text{Hg}^{2+} + \text{Sn(II)} + 2\text{Cl}^- \rightarrow \text{Hg}_2\text{Cl}_2 + \text{Sn(IV)} \quad (3.2)
\]

Zimmermann-Reinhardt reagent was added into solution to avoid other unexpected reaction (Sn²⁺ with MnO₄⁻) prior to titration with KMnO₄. Titration was ended at end point titration as shown by color change to light pink like the color as shown in Figure 3b.

In gravimetric method, iron was precipitated with ammonium hydroxide then precipitate a long with the filter paper were calcinated. All flammable materials were burned and iron hydroxide (reddish brown) was converted into iron oxide (black). The completeness of calcination as shown in Figure 4 (a-b). Iron content based gravimetric analysis was 34.82%. The iron content in pure iron powder was 98.8193%. The iron content analyzed by several methods was tabulated in Table 2.

Based on AAS method, the iron content was 60.49% which is the highest compared to other methods. The AAS method accuracy was 99.51% when it is calibrated with pure iron powder.
concentration. Data obtained from volumetric analysis, the iron content was only 55.33 wt%, with accuracy 96.41%.

Figure 3. Color change at the end point titration (a) MnO$_4^-$-C$_2$O$_4^{2-}$, (b) MnO$_4^-$-Fe$_{2+}^2$

Figure 4. (a) Iron hydroxide (before calcination), (b) Iron oxide after calcination

The AAS finding is closed to previously reported from sample in the same location, which 81% of Fe$_2$O$_3$ or 56% Fe [5]. The iron content in Lampanah iron sand sample was in range of the content in same type sample in Sulawesi which is reported in range of 51.88 – 61.83 wt% based on XRD analysis methods [6]. However the iron content is much higher than in the iron sand of black sea which was reported only 15-16 % of Fe$_2$O$_3$ [15].

UV-Vis, Gravimetric, XRF analysis method gave much lower iron content which only 39.58 wt%; 34.82 wt%; 43.0 wt% respectively. Although accuracy in UV-Vis method was 99.26 % but the iron content in iron sand was only 39.58 wt%. This is might be due to different stability color of complex iron-cynide between the sand and standard samples. It is a phenomenon of experimental error indicator. It is common also AAS method detect iron ion higher than UV-V is spectrophotometer method as reported by [16].

Table 2. Comparison iron content in iron sand sample from different analysis method

| No. | Analytical Methods                                      | Fe content (wt%) | Accuracy* (%) |
|-----|---------------------------------------------------------|------------------|---------------|
| 1.  | UV-Vis spectrophotometer at 480 nm, using KSCN as complex agent | 39.58            | 99.26         |
| 2.  | Gravimetric                                             | 34.82            | 98.82         |
| 3.  | AAS (248.3 nm, air-acetylene, 5A cathode lamp, 0.2 nm split) | 60.49            | 99.51         |
| 4.  | KMnO$_4$ Titration                                      | 55.33            | 96.41         |
| 5.  | X-ray fluorescence (XRF)                               | 43.0+0.17        | NA            |

*calibrated to pure iron sample (Merck)

4. Conclusion

Based on calibration experiment by analysing pure iron powder with AAS, UV spectrophotometric, gravimetric and redox titration methods, then the accuracy analysis percentage of each was 99.51; 99.26; 98.82; 96.41 respectively. The iron contents in Lampanah-Lengah iron sand was significantly different among the analysis methods that were 60.49%, 39.58%, 34.82%, 55.33% and 43.0% detected by AAS, UV spectrophotometric, gravimetric and redox titration methods respectively. AAS methods was confirmed as the most accurate method for iron content determination in iron sand sample. The Lampanah-Lengah iron sand contained high iron content that was 60.49 wt% with accuracy of 99.51%. The iron content in iron sand sample based on the AAS method was comparable to the common content of iron sand reported in other places in Indonesia.
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