Chapter 6

Enrichment with the Morin Ligand of Titanium Element from Waste Ash in Galvanising Factories

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Abstract

In this study, it is aimed to determine the amount of titanium (Ti) in waste ash samples taken from galvanizing factories by using flame atomic absorption (FAAS). In addition, in these wastes, zinc (Zn), silicon (Si), nickel (Ni), manganese (Mn), iron (Fe), chromium (Cr), cadmium (Cd), aluminum (Al), lead (Pb) elements are also the method is intended to be determined.

Different solvent mixtures were tried to prepare the ash samples for analysis and sonication assisted extraction (SAE) device was used at this stage. Morine ligand and Triton X-100 as surfactant was used for the recovery of Ti. The optimum results found were applied on ash samples. As a result of the study, while the optimum recovery values varied between 96-99% , the relative standard deviation values were found to be less than 10%. The enrichment factor and the recovery value in real samples were found to be 45 and 83%, respectively.

1. Introduction

Nowadays, there is a great tendency towards the utilisation of waste materials. The waste ash used in this study is one of the wastes from the galvanising industry and it is used in the industry because it contains high amounts of zinc. However, high value elements such as Titanium (Ti) in galvanising ash, which also contains other metals, are excluded from the evaluation. For these reasons, an alternative method has been developed for the utilisation of galvanising waste for industrial use.

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https://doi.org/10.58830/ozgur.pub132.c582

Ti, which is rarely found in nature, is the most abundant element after aluminium, iron and magnesium in the earth's crust at a rate of 6 per thousand. Ti is one of the transition metals with atomic number 22, located in the d orbital of the 4th period of the 4th period of the 4B group in the periodic table [1-2].

The rarity of ore distribution and the difficulty of obtaining Ti from its ore make it an expensive metal. Ti element, which is widely distributed in the earth's crust, is found in rutile (TiO_2), ilmenite ($FeTiO_3$), titanomagnetite ($Fe_3O_4.TiO_2$), perovskite ($CaTiO_3$), etc. It is one of the various important sprouts and is also found in alluvial-volcanic rocks and sediments formed from them. Sediments may contain heavy metals in the range of 3-12%, usually consisting of ilmenite, rutile, leucoxene, zircon and monazite [3-4].

Ti and its alloys provide excellent services in various industries. In the 21st century, the commercial and industrial use of Ti has matured, but new technologies and applications continue to develop. The density of Ti is only 60 per cent of that of steel or nickel-based alloys. Tensile strength is much better than many stainless metals. Commercial Ti alloys have a higher melting point than steel alloys. Non-magnetic Ti has good heat transfer properties and its coefficient of expansion is lower than that of steel and aluminium. While the aerospace sector accounts for a significant portion of Ti production, it finds use in many fields, including biomedical engineering, marine and chemical applications, automotive and sports equipment [1-7].

Although Ti is as strong as some steels, its density is only half that of steel. It is a widely used element in the aerospace industry in airframe construction, jet engines, missiles, power generation, automotive, chemical and petrochemical industries, shape memory polymeric materials, sports equipment, dentistry (as implant material, etc.), medicine and nuclear fusion reactor construction [6]. It is also used extensively in biomedical materials, especially due to its biocompatibility, non-corrosiveness and processability [7]. In addition, it is also used in flame retardants, insulation materials, rubber, leather and textile industries [8].

The zinc coating method applied to the surface to prevent corrosion on metals is called galvanising. In this study, galvanising ash, i.e. ash containing high zinc content, which is used for the production of zinc and is used as waste, is used. Zinc ash is formed during various processes of galvanising metal sheet or pipe. The galvanising process generates large quantities of waste containing high amounts of zinc, such as from casting, smelting and other metal industries [9 □ 14]. In the galvanising process, zinc and nickel are commonly used for metallic coating, but cadmium, copper, tin, chromium, gold and silver metals are also used [14]. Since the waste ash generated after the galvanising process may contain precious metals, it should be evaluated.

The aim of this study was to develop a new sample preparation method based on emulsion-diffraction extraction (EKE) with Triton X-100 emulsion agent using morin ligand prior to the determination of Ti metal by FAAS and to develop a method for the determination of Ti element in galvanised ash, a galvanised waste. In addition, before the experimental study, different solvent mixtures were tried to prepare the ash samples for analysis and optimum conditions were determined.

2. Material and Experimental Method

In the recovery study of Ti in galvanising wastes using morin ligand have been determined to Ti and other metals by using Agilent brand flame atomic absorption spectrometer (FAAS). Instrumental variables related to the measurements are given in Table 2.1. Other auxiliary materials used are: Sound waves-assisted liquid extraction device (ISOLAB brand), Centrifuge (Hettich EBA III brand), Vortex (Wisemix, Vm-10, Wisd brand), Ultra pure water device (ELGA brand), Analytical balance (Shimadzu, 0.1 mg precision) etc. The chemicals used in the experiment were of Merck quality and all were of analytical purity.

Table 2.1. Parameters related to the measurement of Ti

Wavelength (nm)	Slit width (nm)	Lamp current (mA)	Acetylene flow rate (L/min)	N_2O flow rate (L/min)
364.3	0.5	20.0	6.5	11.00

2.1. Preparation of Standard Solutions

Stock and dilute solutions were prepared at known concentrations to obtain the calibration graphs used in the quantitative analysis. Standard solution was prepared for Ti metal and analysed for Ti by FAAS. The standard of Ti was 1000 mg/L standard NIST (National Institute of Standard and Technology, primary standard substance) stock solution. From the 1000 mg/L stock solution, appropriate intermediate stock (50 mg/L) solution was prepared. Then, from these intermediate stock solution, standard solution was prepared in the range of 1-25 mg/L for Ti.

2.2. Recovery of Ti Element by Morin Ligand

Galvanised waste ash (0.25 g) was firstly solubilised in 20 min using SAE with a mixture of $HCl:HNO_3:H_2O_2$ (1:3:2, v:v:v) which provides maximum solubilisation in the solubilisation specified by Dağcı et al. [15]. In the method validation, optimum conditions were determined by performing recovery studies on the model solution by adding 25μL Ti (from 25 ppm). After the optimum conditions were determined, application was made to real galvanised waste ash. The solubilised waste ash samples were made up to a final volume of 10 mL and enrichment with morin ligand was carried out.

The selection of a suitable sample preparation procedure is one of the most critical steps in the determination of elements using atomic spectrometric techniques [16-18]. The aim of this study was developed a new sample preparation method added Triton X-100 emulsion agent using morin ligand prior to the determination of Ti metal by FAAS and to develop a method for the determination of Ti element in galvanised ash, a galvanised waste. The main variables affecting the EKE method, pH of the sample solution, amount of morin used as ligand, amount of surfactant Triton X-100, extraction time, matrix ion effects were optimised. When calculating the reaction yield [18];

$$yield\% = \frac{Actual\ yield}{Theoretical\ yield}.100$$ equation was used.

After being subjected to the enrichment process steps, the yields were calculated by using the absorbance values read in FAAS. Based on the data, graphs and charts were obtained.

3. Results and Discussion

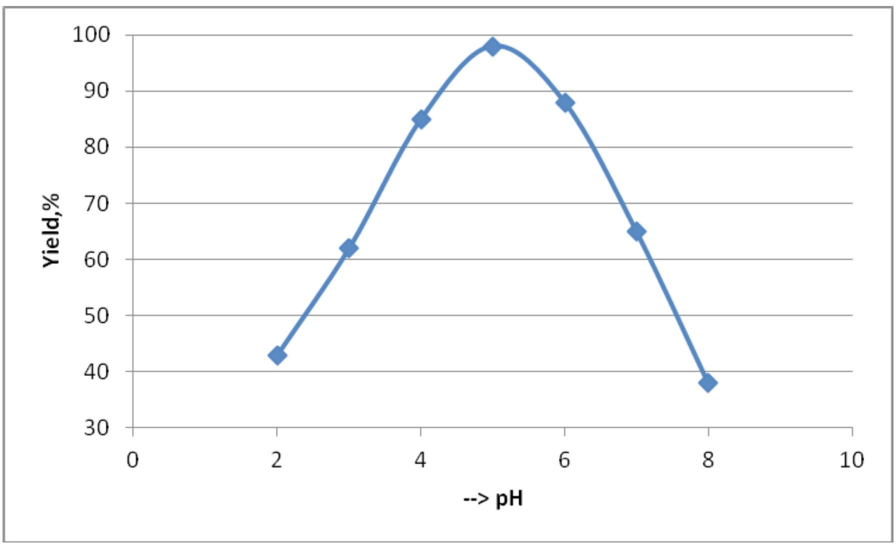
The enrichment of Ti was carried out according to the procedure described in the experimental section and the % yield was calculated with the equation given above and the graphs among Fig 3.1-3.4 were obtained. The calibration range obtained for Ti was 1-25 mg/L, the calibration equation was y = 0.0009x + 0.0022 and the regression coefficient was 0.9991. Important parameters such as pH effect, ligand amount, Triton X-100 amount were investigated in the recovery of Ti with Morin ligand.

3.1. Morin ligand-Ti recovery study

3.1.1. pH Effect

The pH value plays an important role in metal chelate interaction and subsequent extraction steps. The pH was adjusted to seven different pH values selected between 2-8 and the variation of the amount of adsorbed Ti at the end of 20 min with pH was examined and the results are given in Fig 3.1. Model solutions containing Ti on morin ligand and Triton X-100 were prepared to determine the appropriate pH range. The pH of the solutions were adjusted to the desired values with dilute NaOH/HCl. As shown in Figure 3.1, the best recovery effect was obtained at pH 5.00 for Ti. Therefore, the pH of the model solution used in the optimisation studies was set to 5.00.

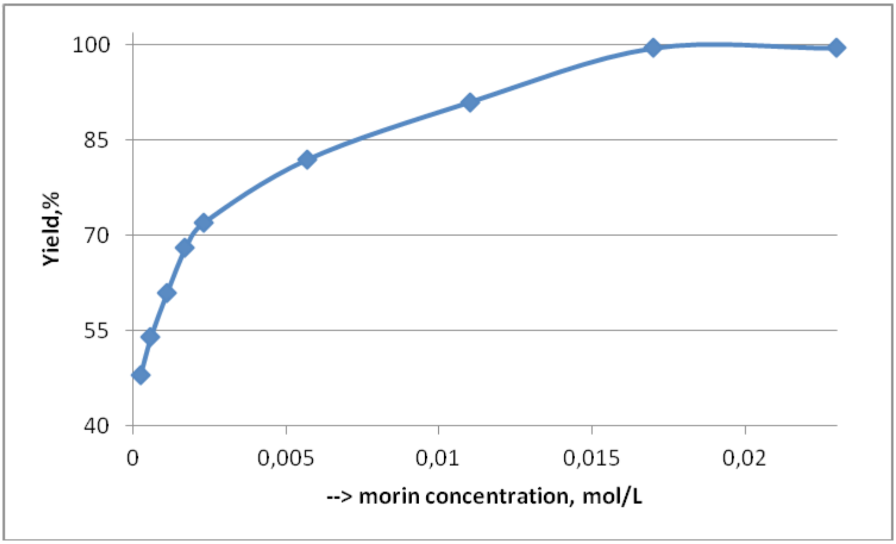
Figure 3.1. Determination of the optimum pH range.(1.15 mg/L Ti standard; morin content 0.017 M; 0.002% Triton X-100; time 20 min; pH range 2-8).



3.1.2. The Effect of Ligand Amount on Recovery

The amount of ligand used is very important for the quantitative recovery of metal ions. As can be seen in Fig 3.2, recovery values were obtained using 0.023; 0.017; 0.011; 0.0057; 0.0023; 0.0017; 0.0011; 0.00057; 0.00023 mol/L morin ligand. Based on these values, 0.017 mol/L was found to be the optimum value for morin ligand with Ti recovery of 99.0%.

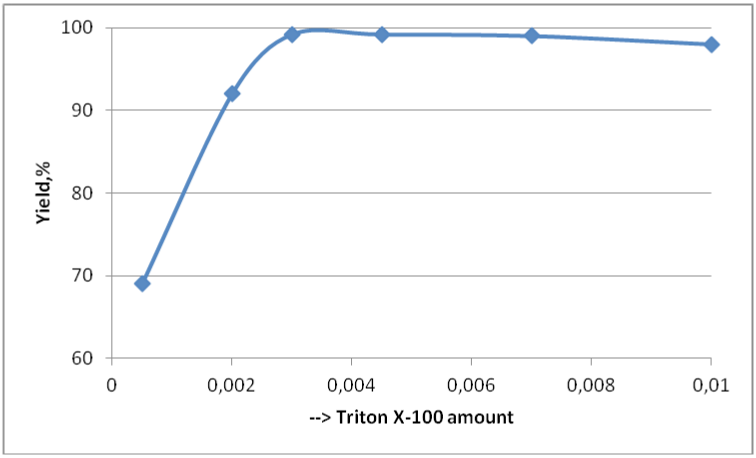
Figure 3.2. Determination of the optimum amount of morin ligand. (pH = 5; 1.15 mg/L Ti standard; 0.002% Triton X-100)



3.1.3. The Effect of Triton X-100 Amount on Recovery

For a successful emulsion diffraction point extraction, it will be necessary to maximise the extraction efficiency by minimising the phase volume ratio of the surfactant to be used [16-17]. The effect of surfactant concentration on extraction efficiency was investigated in the range of 0.0005-0.01 %. The results are shown in Fig 3.3. It was proved that at 0.003% (v/v) concentration of Triton X-100, Ti was effectively extracted from galvanised waste. With increasing Triton X-100 concentration above 0.0045%, an increase in the overall analyte volumes and a decrease in the signals due to the viscosity of the surfactant phase were observed. The optimum surfactant concentration used for Ti was decided to be 0.003% Triton X-100 at the optimum condition with the highest possible extraction efficiency, and for the further optimisation study the amount of Triton X-100 was taken as 0.003% Ti optimum value.

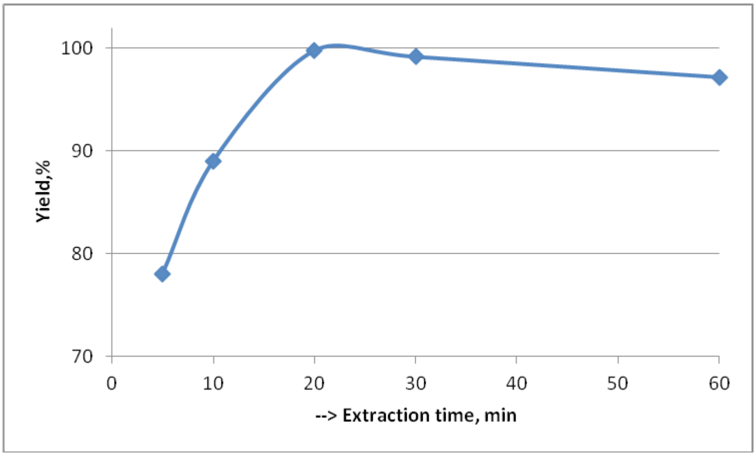
Figure 3.3. Determination of the optimum amount of Triton X-100. (pH = 5; 1.15 mg/L Ti standard; 0.017 mol/L Morin)



3.1.4. The Effect of Time on Recovery

Studies were carried out at room temperature to determine the appropriate stirring time. Extraction efficiency versus extraction time, 5-60 minutes time range was analysed. The % efficiency was calculated from the values found and the % efficiency versus stirring time was plotted. The results obtained are given in Fig 3.4. As can be seen from the figure, the best stirring time for Ti was found to be 20 min and it was decided to use this time in future optimisation studies.

Figure 3.4. Graph of the effect of extraction time on reaction yield. (pH = 5; 1.15 mg/L Ti standard; 0.017 mol/L Morin; 0.003% Triton X-100)



3.1.5. The Effect of Matrix Ions on Recovery

In order to examine the effect of matrix ions on the recovery, the solubilisation process was carried out using the acid mixture and time (maximum dissolution at 20 minutes with $HCl:HNO_3:H_2O_2$ (1:3:2) mixture), which gave the highest concentration result for the optimum amount of solubilised Ti in SAE extraction for galvanised ash [15]. For the recovery of Ti in the solubilised sample, the optimum conditions found in the appendix were applied and analysed by FAAS [15-18]. The recovery efficiency result obtained for Ti was found to be 88%. The enrichment factor was determined as 45 times.

4. Conclusions

In this study, galvanised ash, which is used for zinc production and used as waste, is used, i.e. ash containing high zinc content. Since the waste ash after the galvanising process can contain precious metals, it is foreseen that this waste should be evaluated. For this purpose;

- Method validation and optimisation using FAAS for the analysis of total Ti in waste ash used in galvanising process,
- SAE device (with time optimisation), which is fast and effective in preparing samples for analysis [15],
- Testing different solvent mixtures to prepare ash samples for analysis and determining the best solvent/solvent mixture [15],
- Pre-concentration using morin ligand for the recovery of Ti,
- The application of the found optimum results to real examples has been tried.

For the recovery of Ti, morin ligand and surfactant (Triton X-100) were used. The optimum results were applied to real samples. When using SAE, the samples were prepared using 50 mL falcon centrifuge tubes, because when working in large containers, the velocity of the incident wave would decrease when interacting with the sample and thus the solubilisation process would not be at the desired level. For these reasons, a separation/conversion method was developed for the determination of metals (Cr, Si, Ni, Pb, Cd, Cd, Fe, Zn, Al, Ti, Mn) by flame atomic absorption spectrometry using different acid/acid mixtures for solubilisation by SAE and also by EKE of titanium with morin ligand-surfactant. Ti ions were complexed with morin, then the surfactant Triton X-100 was added and interacted by SAE. The variables such as pH, ligand amount, surfactant amount, surfactant amount, time which affect the accuracy and precision of the intended method were optimised and determined by FAAS. The optimised method was applied to galvanising waste.

Variables such as pH, ligand amount, surfactant amount and time play an important role in metal-chelate interaction and extraction steps. For Ti determination, pH 5.00, 0.017 mol/L morin, 0.003% Triton X-100 and 20 min extraction time were determined as optimum conditions. Optimum recovery values ranged between 96-99%, while relative standard deviation values were less than 10%. The enrichment factor and recovery value in real samples were found to be 45 and 88%, respectively. It is thought that the oxide compounds in the galvanising waste ash used in this study also act as adsorbents.

The adsorption application of metal alone, metal-morin complex and morin ligand on galvanised waste and very successful results (88% efficiency) were obtained for solutions containing the mixture. The used galvanising ash was also proved to be usable as adsorbent material. The results obtained from this study may contribute to environmental risk analysis studies specific to heavy metals in the environment where galvanising wastes are used.

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