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Optimization of a Rapid Chromatographic Method for Separation and Determination of Titanium Simultaneously with Iron in Different Geological Samples using Ion Chromatography

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ABSTRACT

In this study, a rapid and selective chromatographic method has been optimized for the simultaneous separation and determination of titanium(IV) and iron(III) using High-Performance Ion Chromatography (HPIC). A CS5A analytical column was employed under optimized isocratic conditions, where separation was achieved within 7 minute s using a 7 mM pyridine-2,6-dicarboxylic acid (PDCA) eluent at pH of 1.9 and a flow rate of 0.9 mL/min. Detection was carried out using UV absorbance at 308 nm. The method demonstrated high sensitivity and reproducibility, making it suitable for routine analysis. To ensure accuracy and reliability, the optimized method was validated using a certified soil sample approved by the China National Analysis Center of Iron and Steel (Beijing, China). The validated procedure was also successfully applied to the analysis of two real geological samples collected from Gabal El Sela and Aswan regions in Egypt, demonstrating its effectiveness for trace metal analysis in complex matrices. This approach provides a simple, cost-effective, and efficient alternative for the simultaneous determination of multivalent metal ions in environmental and geological studies.

1. Introduction

The ninth element, titanium (Ti), is one of the most abundant in the Earth's crust. Because of its unique properties—lightness, high strength-to-weight ratio, and inertness to many corrosive substances—its metal has come to be recognized as a space-age material [1,2,3]. The spontaneous formation of a thin, durable, and protective oxide layer on the metal's surface contributes to its excellent corrosion resistance, biocompatibility, and chemical inertness [4]. As a result, titanium and its alloys are widely employed in chemical processing, and as implant components that can be anchored directly or after the development of β-Ti alloys into human bone tissue [5,6].

Compounds of titanium(IV) are also critical in industry and scientific research. Titanium finds applications in medicine, pharmacology, cosmetics, and jewelry [7]. According to Fink (2005)[8], titanium is commonly alloyed with aluminum to refine grain size, with vanadium and copper to enhance hardness, with steel as ferrotitanium for use as a deoxidizer, and in stainless steel to reduce carbon content. Aside from its vast industrial applications, titanium has substantial biological effects on plants and is considered a necessary micronutrient, where it regulates nitrogen metabolism [9,10].

Considering the significance of titanium, there is a strong analytical need to establish straightforward, highly sensitive, and dependable techniques for detecting trace levels of titanium across different sample types, even in the presence of interfering ions. A range of analytical approaches has been employed, such as photometry [9], spectrometry [11], spectroscopy [12,13], spectrophotometry [14,15], and voltametry [16]. The majority of these techniques are costly and require extreme caution during use, and it is frequently challenging to directly determine Ti(IV) at very low concentrations due to the techniques' inadequate sensitivity and matrix interferences present in real samples. High Performance Ion Chromatography (HPIC) and High Performance Liquid Chromatography (HPLC) [17] are promising techniques for the separation of polyvalent metal cations by introducing appropriate complexing agents in the mobile phase [18,19].

This paper describes the investigation of suitable chromatographic conditions for the direct determination of Ti(IV) simultaneously with Fe(III) which ever interfere with most of the analyzing elements due to their high concentrations in different geological samples. The method is achieved using a High Performance Ion Chromatograph (DX-500) and ascertained by a soil-certified sample (NCSDC 73325).

2. Experimental

2.1. Instrument

Separation and determination of titanium simultaneously with iron were performed by using High Performance Ion Chromatograph (HPIC), Dionex DX-500 (Sunnyvale, CA, USA) Fig. (1). The pH readings were picked up using a digital Jenway pH meter. (UK).

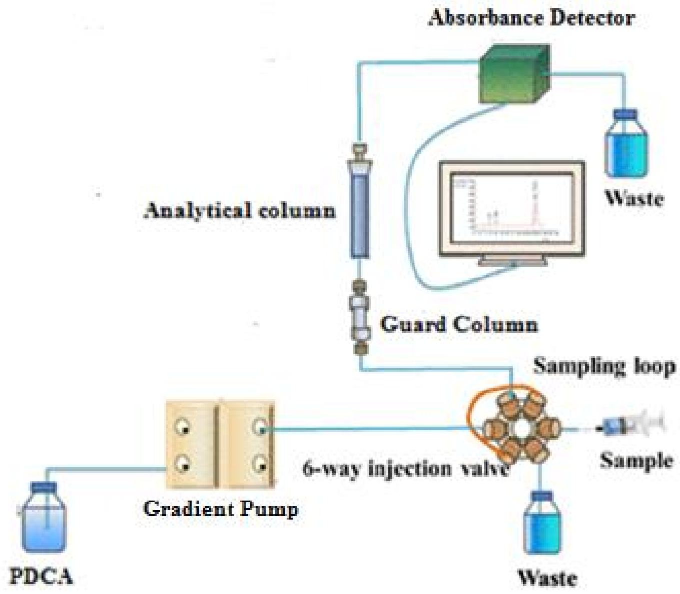

Figure 1: Schematic diagram for High Performance Ion Chromatograph (HPIC), Dionex DX-500

2.2. Reagents and Solutions

Chemicals utilized in this work were of analytical grade. Nanopure water (**18.2**MΩ-cm) (Thermo Fisher Scientific Inc., USA) was used to prepare all the solutions. Ti(IV) (99.9%) and Fe(III)1000mg/L (d= 1.09g/cm^3) from Fluka, Buchs, Switzerland were used where their test solutions were prepared by diluting appropriate amounts in nanopure water. Mobile phase of Dipicolinic acid (DPA) [pyridine-2,6-dicarboxylic acid (PDCA) Merck, Germany] of purity 99% has been applied.

2.3. Recommended Chromatographic Procedure

Isocratic elution using 7mM PDCA of pH 1.9 has been achieved for the separation and determination of Ti(IV) and Fe(III) via (HPIC). The flow rate of the mobile phase solution was adjusted at 0.9 mL/min. with the chosen wavelength of 308nm.

2.4. Samples Characterization

The optimized advanced procedure was applied for the determination of Ti(IV) and Fe(III) in a pair of geological samples of different contents and localities in addition to a certified soil sample (NCSDC 73325) approved by China National Analysis Center of Iron and Steel, (Beijung, China). These geological samples involved granite sample from Gabal El Sela and another Granodiorite sample from Aswan, Egypt. El-Sela shear zone. It lays at about 22 km SW of Abu-Ramad city. It is bound by Latitudes 22°17′44″ - 22°18′10″ N and Longitudes 36°13′28″ - 36°14′27″ E [20] Granodiorite sample was collected from Egypt's Eastern Desert of Aswan, near Gabel Abu Marwa which is located between 23°00′ and 23°10′ north latitudes and 33°17′ and 33°28′ east longitudes [21].

2.5. Samples Digestion

0.5g of the certified soil sample and each of the other two geological samples were grinded to -200 mesh and digested in mixtures of concentrated acids (hydrofluoric, nitric, sulfuric and perchloric) till dryness. The obtained residues were then dissolved in HCl (1:1) and the mixtures were gently heated and cooled to room temperature and then diluted to 50mL using nanopure water (18.2 mΩ-cm). From each of the generated aliquots, 50 µL were taken for titanium and iron analysis using the suggested method under the specified optimal approaches.

3. Results and Discussion

In order to investigate the main target of this work which is directed towards the creation of a simple, sensitive and accurate method for the separation and determination of Ti(IV) and Fe(III) in a variety of samples using HPIC, the influence of various effective parameters including; wavelength detection beside PDCA eluent pH, concentration, and flow rate in addition to the effect of the interfering cations has been studied.

3.1. Analytical Conditions Optimization

3.1.1. Wavelength Detection

Under hypothetical conditions of PDCA eluent pH, concentration, and flow rate, the wavelength of the absorbance detector (AD20) for the determination of Ti(IV) and Fe(III) was tested across the UV range of 200-400nm. Apparently, it was observed that Ti(IV) and Fe(III) eluted at 200 nm; however, the separation efficiency was poor, as indicated by the low peak areas corresponding to their concentrations. By increasing the wavelength gradually, an increase in their area under peak was observed until a maximum was reached at 308nm wavelength after which a decrease was detected and progressively no peaks were eluted anymore. So, 308nm was chosen to be the optimum wavelength at which Ti(IV) and Fe(III) will be determined.

3.1.2. Effect of PDCA Eluent pH

The influence of eluent pH on the chromatographic response of Fe(III) and Ti(IV) complexes was systematically studied in the pH range from 1.0 to 3.0 using 7 mM pyridine-2,6-dicarboxylic acid (PDCA), a flow rate of 0.7 mL/min, and UV detection at 308 nm. As illustrated in Figure 2, both analytes exhibited pH-dependent behavior, with a pronounced difference in response magnitude and optimal pH between Fe(III) and Ti(IV).

The chromatographic behavior of Ti(IV) and Fe(III) was significantly influenced by the pH of the PDCA eluent. Both metal complexes showed increasing peak areas with rising pH, reaching optimal response at pH of 1.9. This trend is attributed to enhanced ligand deprotonation, which promotes stronger metal-ligand coordination. Beyond pH 1.9, signal intensities declined, likely due to complex instability or competition with hydroxide ions. Despite of Fe(III) having a higher injected concentration than Ti(IV), both metals exhibited maximum detection at the same pH, supporting the selection of pH 1.9 as the optimal condition. The CS5A column's mixed-mode functionality further aided in stabilizing and resolving the metal-PDCA complexes efficiently.

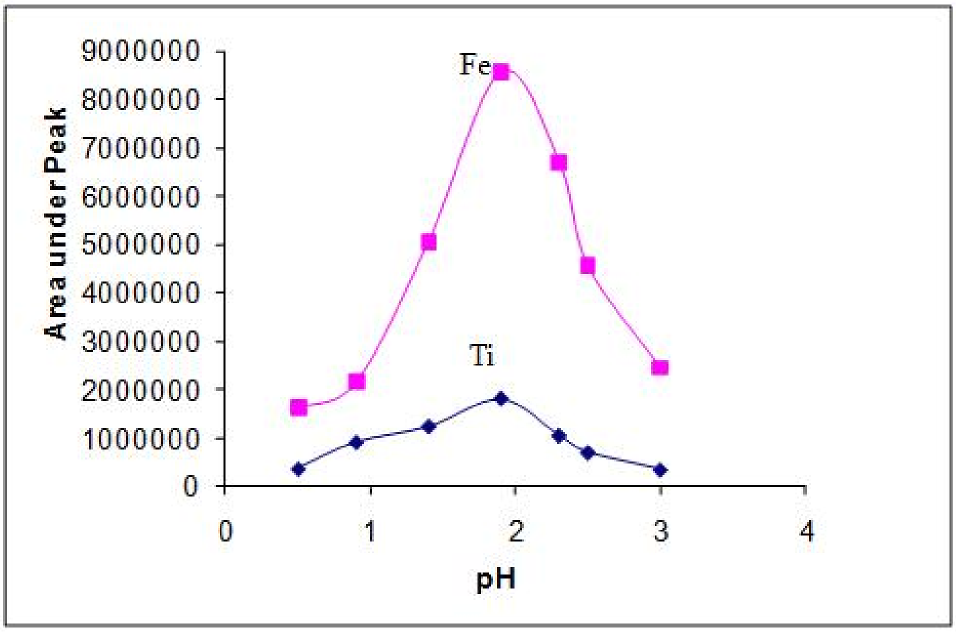

Figure 2: Influence of pH on area under peak of Ti(IV) and Fe(III)

3.1.3. Effect of PDCA Eluent Concentration

The concentration of the complexing agent (PDCA) plays a pivotal role in the chromatographic separation of Ti(IV) and Fe(III). As shown in Figure 3, increasing the PDCA concentration from 3 to 7 mM resulted in a progressive enhancement in the area under the peak for both metal ions, indicating improved complex formation and detection sensitivity. This is attributed to the increased availability of PDCA ligands that effectively chelate with Ti(IV) and Fe(III), leading to more stable and detectable complexes.

The response plateaued or slightly declined beyond 7 mM, particularly for Fe(III), suggesting a saturation point beyond which excess PDCA may not further improve complexation or might even cause competitive interactions that reduce detector response. Therefore, 7 mM PDCA was identified as the optimal eluent concentration, balancing complexation efficiency and chromatographic resolution. Notably, Fe(III) consistently exhibited a higher peak area than Ti(IV), consistent with its higher injected concentration and potentially stronger affinity to PDCA under the tested conditions.

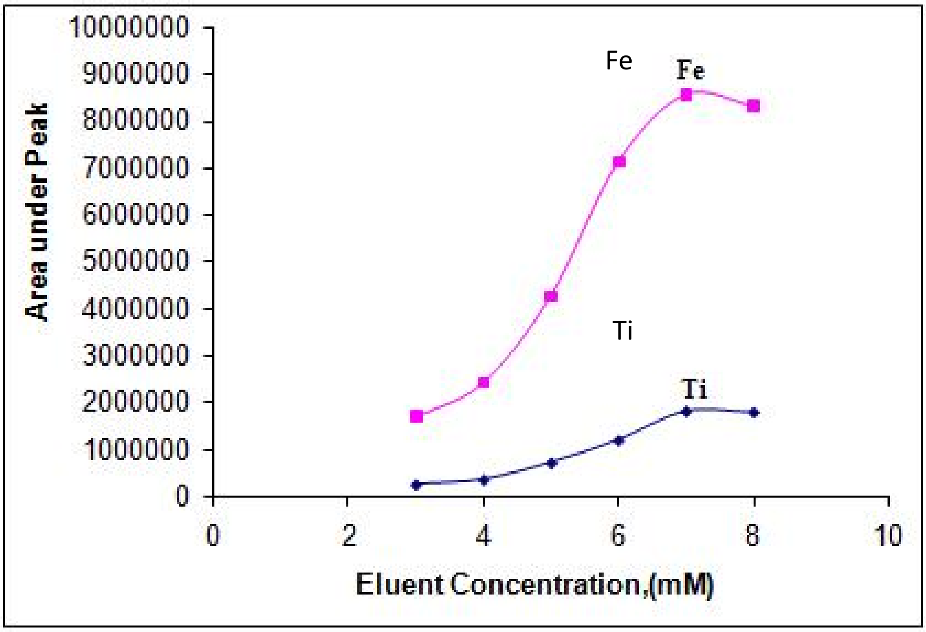

Figure 3: Influence of PDCA eluent concentration on area under peak of Ti(IV) and Fe(III)

3.1.4. Effect of PDCA Eluent Flow Rate

To achieve maximum separation and sensitivity for Ti(IV) and Fe(III), the influence of PDCA eluent flow rate was evaluated across the range of 0.1–1.2 mL/min. As shown in Figure 4, the area under the peaks for both metal complexes increased progressively, reaching maximum values at a flow rate of 0.9 mL/min. This indicates an optimal interaction time between the Ti–PDCA and Fe–PDCA complexes and the functional groups of the CS5A column, which is packed with both cationic and anionic exchange resins. The enhanced mass transfer and reduced band broadening at this rate likely contribute to better signal intensity and sharper peaks.

Beyond 0.9 mL/min, a noticeable decline in peak area was observed for both ions. This behavior can be attributed to insufficient residence time of the complexes in the column, resulting in reduced retention and incomplete resolution due to deficient interaction with the stationary phase. Furthermore, higher flow rates may hinder the equilibrium between mobile and stationary phases, resulting in reduced sensitivity and lower detection efficiency.

Based on these observations, a flow rate of 0.9 mL/min was selected as optimal, offering a balance between high analytical response, resolution, and run time, while maintaining reproducibility and column performance.

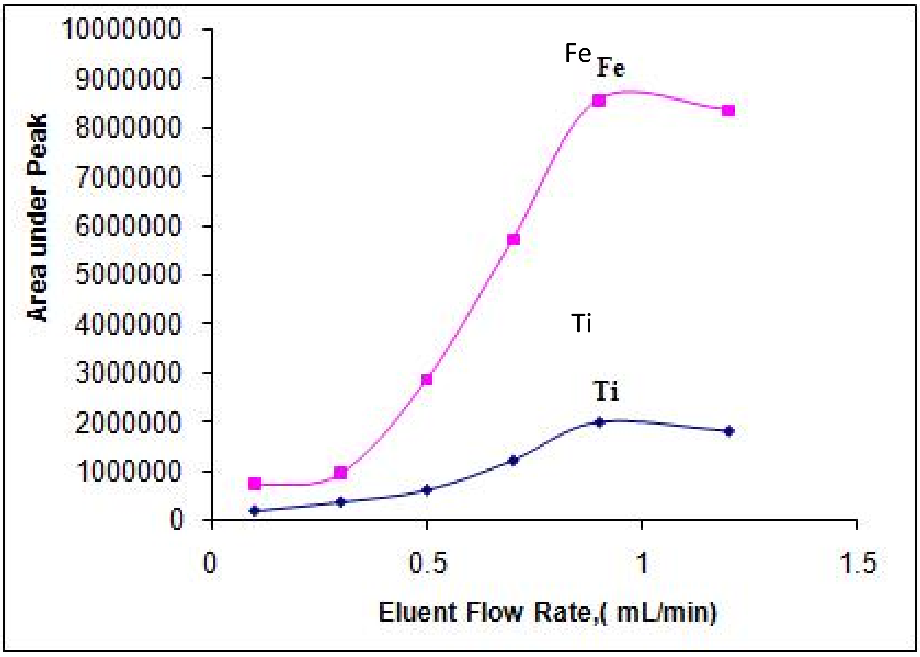

Figure 4: Influence of PDCA Eluent Flow Rate on the Peak Area of Ti(IV) and Fe(III) Complexes

3.1.5. Effect of Diverse Ions

To assess the potential analytical applications of the suggested approach, the effect of several foreign ions found in diverse geological samples was investigated. Since Ti(IV) and Fe(III) were separated and determined by complexation with PDCA, it was important to study the interference of the separated elements with other cations. As it well known, that the PDCA mobile phase has the ability to elute certain cations

[22], no interferences were observed under the optimized chromatographic conditions, as demonstrated in Figure 5.

In this investigation, a number of potential interfering ions-including Cu, Ni, Cd, Co, and Mn-were deliberately introduced at relevant concentrations to simulate natural sample complexity. Remarkably, among all tested ions, only Fe(III) was detected and eluted under the studied conditions. This highlights the high selectivity of the PDCA eluent and CS5A column, particularly for Fe(III) and Ti(IV), while effectively suppressing signals from other common multivalent ions.

It is important to emphasize that the primary objective of this study was the efficient and selective separation of Ti(IV) from complex geological matrices. However, due to the fact that Fe(III) was the only ion co-eluted under the applied conditions, it became essential to simultaneously optimize the chromatographic method for Fe(III) as well. The co-elution and clear resolution of Fe(III) alongside Ti(IV) not only validated the performance of the separation method but also demonstrated its practical utility in real sample analysis where Fe is naturally abundant.

The observed stability of the Ti–PDCA and Fe–PDCA complexes, coupled with the resolving power of the CS5A column, contributed to sharp and interference-free peaks. These findings reinforce the method’s robustness and suitability for routine geochemical analysis, offering reliable quantification of Ti(IV) even in the presence of potentially interfering ions.

The Chromatographic Parameters and Interpretation for Ti(IV) and Fe(III) Separation are inserted in Table(1).

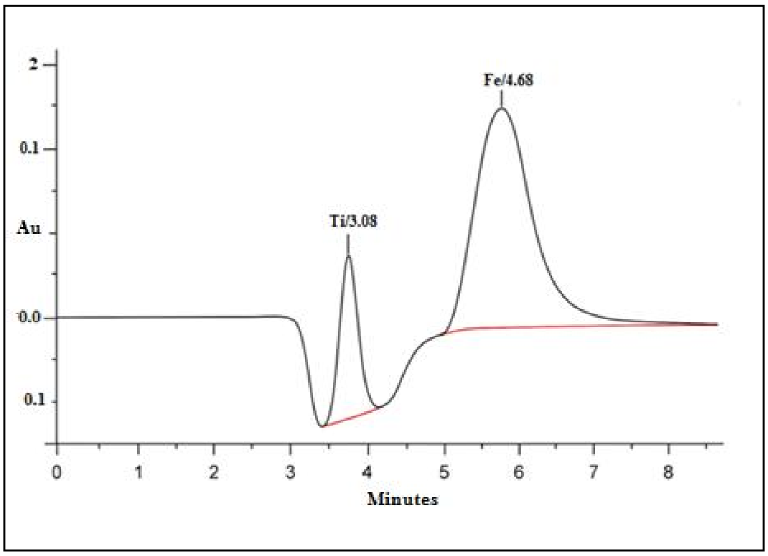

Figure 5: Chromatogram of the studied synthetic Ti(VI) (10 ppm) and Fe(III) (20 ppm) obtained using a PDCA eluent under optimized conditions: detection at 308 nm, pH of 1.9, and a flow rate of 0.9 mL/min.

Table 1: Chromatographic Parameters and Interpretation for Ti(IV) and Fe(III) Separation

Parameter	Ti(IV)	Fe(III)	Interpretation
Retention time	3.08 min	4.68 min	Ti(IV) elutes earlier under the chosen PDCA conditions, indicating moderate interaction with the column.
Peak width (W)	0.30 min	0.50 min	Fe(III) is retained longer due to stronger coordination with PDCA, but still elutes with good separation.
Selectivity (α)	1.52	-	High selectivity confirms distinct separation between Ti and Fe analytes.
Resolution	4	-	Excellent resolution (>1.5); indicates complete baseline separation suitable for quantification
Peak shape	Symmetrical	Slightly broader	Indicates efficient column performance and minimal tailing.
Implication for analysis	Accurate, fast quantification	Delayed but well-separated quantification	The method offers clear, distinct peaks allowing reliable and simultaneous determination.

Although Fe(III) exhibits slightly stronger retention due to its higher affinity with PDCA, the method's design and optimized conditions allow Ti(IV) to be efficiently and selectively separated with sharp peak resolution and baseline separation. The shorter retention time of Ti(IV) reflects its effective elution under the chosen conditions, confirming that the method is highly suitable for rapid and accurate quantification of titanium even in the presence of closely eluting species like Fe(III). This balance between retention and resolution highlights the method's efficiency in separating both metals within a short analysis time, while still prioritizing the accurate detection of Ti(IV)—the primary target of the study.

3.2. Calibration Graphs, Relative Standard Deviations and Detection Limits

The calibration graphs were designed using the recommended procedure for different amounts of Ti(IV) and Fe(III) for the range of 5-20 ppm for Ti(IV) and 5-25 ppm for Fe(III). The resulted regression coefficients assigned were 0.998 and 0.996 for Ti(IV) and Fe(III) respectively with linear relations (Figures 6,7). By calculating the Relative Standard Deviation (RSD) for Ti(IV) and Fe(III), the overall performance of the worked procedure installed through ten injections recorded were ± 0.12 % Ti(IV) and ± 0.10 % for Fe(III). For 50µL injection volume the detection limits stated for Ti(IV) and Fe(III) were about 1 and 0.5 ppm respectively.

From the overall results the proposed method provided rapid isocratic separation of Ti(IV) and Fe(III) within 7 minutes with excellent reproducibility and sensitivity, achieving detection limits of 1 ppm and 0.5 ppm, respectively.

Although pyridine-2,6-dicarboxylic acid (PDCA) has been successfully employed in our previous studies for the chromatographic separation of various metal ions, its continued application is due to its proven high affinity and selectivity for transition and post-transition metals. In the present study, PDCA was specifically optimized at a concentration of 7 mM under acidic pH (1.9) to achieve rapid, efficient, and baseline-resolved separation of Ti(IV) and Fe(III). This combination of parameters—eluent concentration, pH, and detection wavelength at 308 nm—has not been previously reported for the simultaneous quantification of these two elements. The optimized method demonstrates excellent reproducibility, sensitivity, and selectivity in real geological matrices, which supports the suitability and novelty of PDCA in this specific analytical context.

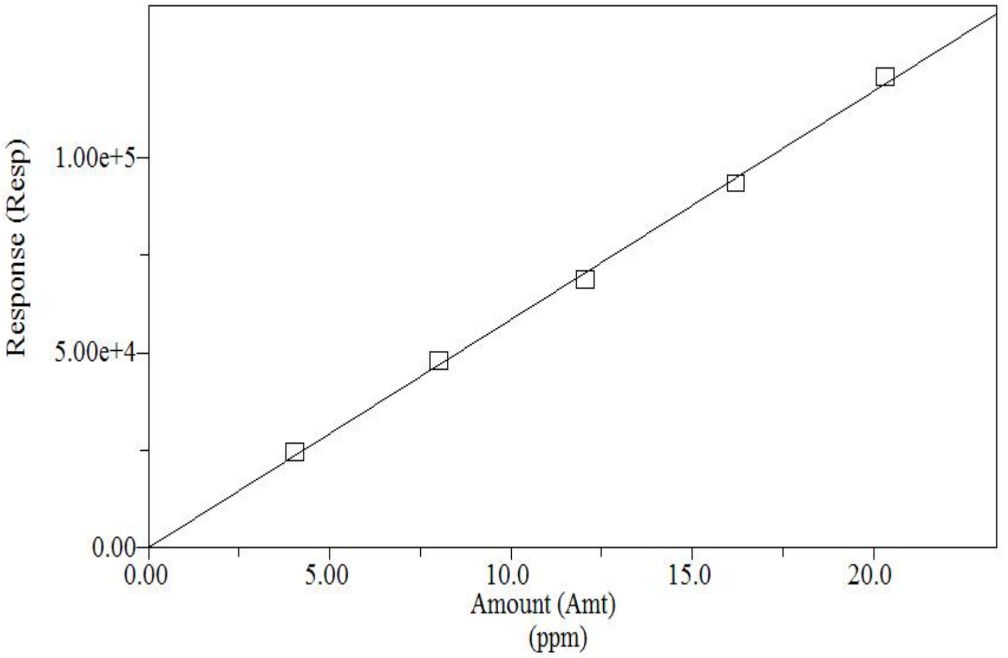

Figure 6: Standard calibration Curve of Ti(IV)

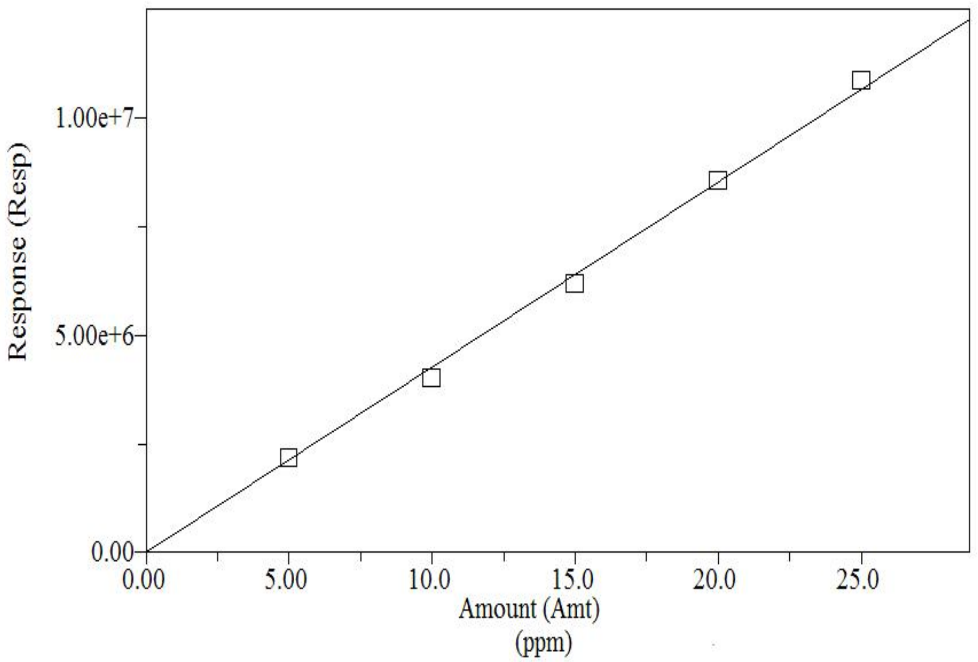

Figure 7: Standard calibration Curve of Fe(III)

3.3. Analytical Applications

To evaluate the practical applicability and reliability of the optimized chromatographic method, it was employed for the determination of Ti(IV) and Fe(III) in real geological matrices. The method was validated using a certified soil reference sample, issued by the China National Analysis Center of Iron and Steel (Beijing, China). Additionally, two representatives geological samples-granite from Gabal El-Sela and granodiorite from Aswan, Egypt-were analyzed under the same optimized conditions.

The concentrations of Ti(IV) and Fe(III) in all samples were successfully quantified, and the results are summarized in Table 2. These findings confirm the method's suitability for accurate and simultaneous determination of titanium and iron in complex geological matrices.

Table 2: Analytical results of Ti(IV) and Fe(III) in Certified Soil Sample (NCS DC 73325), Gabal El Sela Granite and Aswan Granodiorite Samples

Element	Certified Soil Sample (CSS)		Gabal El Sela Granite Sample, (ppm)	Aswan Granodiorite Sample, (ppm)
	Concentration (ppm)	IC Reading (ppm)		
Ti(IV)	20200	20187	750	9700
Fe(III)	65606	65590	4880	91490

4. Conclusion

A selective and rapid ion chromatographic method was successfully optimized for the simultaneous separation and determination of Ti(IV) and Fe(III). Employing pyridine-2,6-dicarboxylic acid as a complexing agent allowed effective separation under isocratic conditions, achieving a total run time of under 7 minutes with a 7 mM PDCA eluent at pH of 1.9 and a flow rate of 0.9 mL/min. Detection was performed via UV absorbance at 308 nm. The method demonstrated high precision, low detection limits, and excellent reproducibility, validated using a certified soil reference material (NCS DC 73325) alongside real geological samples from Egypt. Given its sensitivity, simplicity, cost-effectiveness, and applicability to complex matrices, the proposed method is a valuable tool for routine monitoring of titanium and iron in environmental and geological studies.

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Conflict of Interest: The authors declare no conflict of interest.

Data Availability Statement: Data is contained within the article.

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