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Application of Classical Titration and ICP-OES Techniques for the Determination of Total Iron, Metallic Iron, and Iron (II) as Tools for Assessing the Feasibility of Ferrous Metallurgical Waste Management

Abstract: The introduction of ferrous waste into a technological process requires knowledge of the quantitative fraction of iron at various oxidation levels. The research work discussed in the article aimed to develop an effective strategy for handling the test material in order to obtain information concerning iron speciation, relevant for assessing the reuse potential of ferrous waste. The determination of various forms of iron in metallurgical waste involved the use of titration methods and the ICP-OES technique. The iron content in the waste material ranged from a few to more than 90 %, whereas the proportions of individual forms varied. The test results confirmed the effectiveness of the ICP-OES technique in the determination of total and metallic iron. In turn, the classical methods did not always provide reliable results.

Key words: ferrous (iron-bearing) waste, classical analytics, ICP-OES, iron speciation

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1. Introduction

The production of steel and semi-finished steel products is inextricably connected with the generation of post-production waste. It is estimated that metallurgical processes generate 500 kg of waste for every ton of steel produced [1]. According to European Union guidelines, the aforesaid waste is categorised as hazardous [2–4]. Poland's metal and iron metallurgy produces approximately 37 million tons of waste per year, which constitutes 30 % of the total amount of waste produced. It is estimated that about 80 % of metallurgical waste is recycled [4]. Unused waste is temporarily stored in company and municipal landfills. The long-term storage of waste is costly and carries the risk of environmental degradation. Metallurgical waste is a group of materials varying in chemical and phase composition. The aforementioned diversity results from technological process conditions and the composition of feedstock materials.

Efficient methods of refining ferrous waste can provide valuable raw materials for metallurgy and make it possible to manage environmentally hazardous waste. One of the methods of dealing with the waste involves recycling it back into the metallurgical process as a raw material. In terms of steelmaking waste recovery, the most important component of the waste is iron. Ferrous waste, such as iron slag, blast furnace dust, steel dust, foundry dust as well as scale and scale sludge, can vary significantly as regards iron content, and reach up to 70–80 % [5–7].

The decision to include ferrous waste in the technological process requires knowledge concerning the total iron content as well as the quantitative fraction of the forms of this chemical element in various oxidation states. The assessment of waste usability as well as the monitoring of the efficiency of iron reduction and recovery from ferrous waste materials require the knowledge concerned with the total iron content as well as the content of metallic iron and iron in the second oxidation state.

The identification of the chemical forms of a given chemical element in different oxidation states and the ratios of these forms constitute the subject of speciation analysis. Iron speciation involves the use of several instrumental techniques such as atomic absorption spectrometry (AAS) [8–10], voltammetry [11], inductively coupled plasma optical emission spectrometry (ICP-OES) [12, 13], inductively coupled plasma mass spectrometry (ICP-MS) [14], X-ray fluorescence spectrometry (XRF) [15–18], X-ray diffraction (XRD) and classical titration methods [20–21].

Regardless of the analytical technique used, the primary problem in speciation analysis is related to sample preparation. The issue is particularly relevant for analytical techniques requiring the preparation of solution samples. The application of chemical reagents aimed to decompose the test material entails the risk of chemical reactions distorting the original proportions of chemical element speciation forms. Scientific publications lack information concerning the investigability of iron speciation in ferrous metallurgical waste.

The objective of the research work discussed in the article was concerned with investigating the possibility of determining total iron, metallic iron and divalent iron in ferrous metallurgical waste using ICP-OES and classical titration techniques. The research-related tests aimed to identify methods of dealing with the material, aimed at the obtainment of information concerning iron speciation, constituting the starting point for assessing the recyclability of ferrous waste.

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2. Experiment

2.1. Test material

The iron speciation tests involved ferrous metallurgical waste characterised by varied chemical and mineralogical compositions. The waste samples included sludge, pre- and post-reduction scale, pre- and post-reduction dust as well as slags. The initial test material had various physical structures. The waste was dried to a solid mass and homogenised by grinding. The waste prepared in the above-named manner was sampled for representative analytical samples, corresponding to the average composition of the entire batch of material subjected to analysis.

2.2. Determination of metallic iron in ferrous waste materials

The investigation concerning the determinability of metallic iron in metalliferous waste samples involved the use of titration and ICP-OES techniques.

2.3. Sample preparation for the determination of metallic iron using the titration technique and disodium stannate

The determination of the metallic form of iron necessitated the preparation of the test material by dissolving it in the alcoholic solution of mercury(II) chloride and sodium salicylate. The samples having a mass of 0.5 g along with ethanol (100 cm^3), mercury chloride (4 g) and sodium salicylate (3.5 g) were boiled for an hour in a flat-bottomed flask featuring a reflux condenser. Afterwards, the solution was cooled and transferred to a 200 cm^3 flask and supplemented with ethanol. Next, the mix was filtered through a hard filter (84 g/m^2). Depending on the content of metallic iron, the filtrate was divided into aliquots of 100 cm^3 (if the metallic iron content did not exceed) 30 % or 50 cm^3 (if the content of metallic iron exceeded 30 %). The divalent iron present in the solution was oxidised to trivalent iron using a solution of hydrochloric acid (25 cm^3), ammonium persulphate (15 cm^3) and water (160 cm^3). The titration aimed at determining the metallic iron content involved the use of a solution of disodium stannate and sodium salicylate (as an indicator) at a temperature of 50 °C. The solution was titrated until it underwent discolouration or turned yellow. The confirmation of titration method correctness necessitated the preparation of a series of model solutions, based on pure metallic iron. The weight amounts reflected the elemental content within the range of 1 % to 80 %, in relation to 0.5 g of the sample mass. Regardless of the analyte concentration in the sample, the determinations of metallic iron in the model samples was characterised by low analyte recovery (tab. 1). Xu et al. [13] observed a similar effect and linked it to the formation of a passivation layer on the surface of sample grains. The aforementioned layer, whose formation resulted from the effect of the reaction mixture, blocked the effect of the reagent etching iron in metallic form.

Table 1. Results of the titrimetric determination of metallic iron in synthetic samples with disodium stannate

Assumed Fe content [% w/w]	Weight of pure Fe [g]	Result [% w/w]	Recovery [%]
1	0.005	0.45	45
10	0.05	5.70	57
50	0.25	44.33	89
80	0.45	60.64	76

2.4. Preparation of samples for the determination of metallic iron with the ICP-OES technique and copper sulphate

The preparation of solutions for the ICP-OES technique-based determination of metallic iron involved the extraction of metallic iron from the sample in the ion exchange reaction (1) [22]:

$$\mathrm{Fe} + \mathrm{CuSO_4} \rightarrow \mathrm{FeSO_4} + \mathrm{Cu} \tag{1}$$

The placing of the sample (0.5 g) in a beaker was followed by adding 50 cm^3 of $CuSO_4$ solution along with the same amount of boiled and cooled demineralised water. Afterwards, the beaker was covered and heated for 60 minutes. The content of the beaker was occasionally stirred with a glass rod. Throughout the process, the constant volume of the solution in the beaker was maintained, whereas pH was kept within the range of 6 to 7. The hot solution was filtered into the beaker using a hard filter. Next, the solution was acidified with hydrochloric acid solution until the value of pH was below 1.

The calibration of an OES-ICP Agilent 5100 SVDV spectrometer was based on a series of synthetic calibration (model) solutions. The matrix composition of the synthetic calibration solutions included the presence of copper sulphate. The calibration was performed for the Fe 238.204 nm iron emission line, obtaining a correlation coefficient of more than 0.999 (Fig. 1). The calibration curve allowed the determination of metallic iron in model solutions, following the ion exchange reaction. Within the analyte concentration range of 0.5 % to 90 % (in relation to a sample weight of 0.5 g), the recovery of metallic iron was not less than 90 % (Table 2).

Table 2. Results of the determination of metallic iron content in model solutions obtained using the ICP-OES technique

Assumed Fe content [% w/w]	Weight of pure Fe [g]	Result [% w/w]	Recovery [%]
0.5	0.0025	0.45	90
1	0.005	0.90	90
5	0.025	4.50	90
10	0.05	9.30	93
20	0.10	19.20	96
50	0.25	49.37	99
80	0.40	79.31	99
90	0.45	89.40	99

2.5. Comparison of metallic iron determination results obtained using the titration technique and the ICP-OES technique

A series of metallic iron determinations were performed using certified ICRM-Centre R40 and Euro 685-1 reference materials (Table. 3). The metallic iron content in ferrous waste samples was analysed using both testing methods (Table 4).

The results of the metallic iron determinations obtained using both methods confirmed the presence of the analyte in the waste materials. Among the waste materials tested, the highest values of metallic iron were found in dust samples, where the concentration of analyte reached 75 %. Sludge and scale were characterised by the greatest variation in the proportion of metallic iron fraction. The fraction of the component subjected to determination was restricted within the range of approximately 0.5 % to approximately 80 %. The results of the determinations obtained in relation to the slag samples were characterised by a relatively small range of concentrations of analyte. No interference of metallic iron determinations by Fe (II) was observed in any of the experiments performed within the research work.

In terms of the titration technique, the results obtained in relation to the model samples (pure analyte, without matrix) and those obtained for the certified reference materials were characterised by low recovery values. The above-named effect was also observed in relation to the samples characterised by the higher concentration of analyte. In terms of metallic iron contents below 5 %, the results obtained using the ICP-OES and titration techniques were comparable. The smallest differences between the techniques were observed in relation to the determination of metallic iron in slag samples. Probably, an important factor was the process of waste material formation, in which the metallic form of iron was bound in a form decomposing in the reaction mixture used in titration technique-based determinations. The results indicated the possibility of using the titration technique only in qualitative analysis.

2.6. Total iron determination

The identification of the possibility of determining total iron was performed using two methods. The titration method, in which the titrant was potassium dichromate (VI) [23] and the ICP-OES technique.

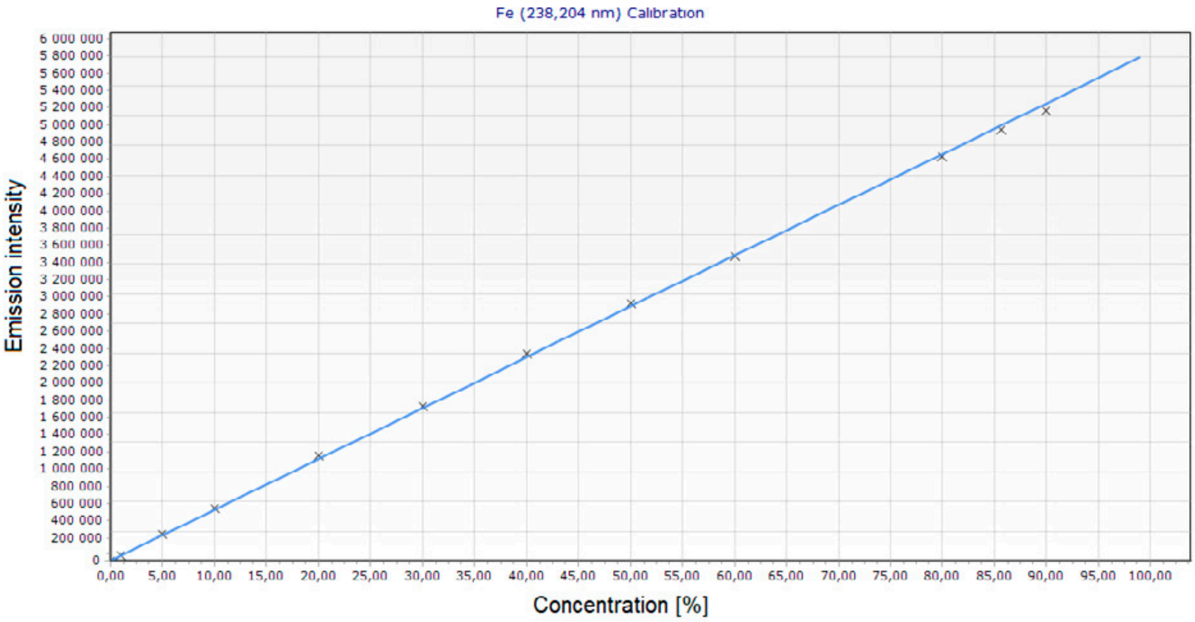

Fig. 1. Calibration curve for an iron line of 238.204 nm

Table 3. Results of metallic iron determination in reference materials, obtained using the titration and ICP-OES techniques

Reference material	Certified value [% m/m]	Titration		ICP-OES	
		Result [% w/w]	Recovery [%]	Result [% w/w]	Recovery [%]
ICRM Centre R 40	85.70	56.96	67	85.54	100
Euro 685-1	80.80	51.20	63	78.27	97

Table 4. Metallic iron content in waste ferrous materials determined using the titration and ICP-OES techniques

Sample name	Material typeV	Metallic Fe content [% w/w]	
		Titration	ICP-OES
697/6	sludge	1.01	0.79
2B-16		42.6	74.55
2A-16		38.6	60.93
697/2	scale	0.39	0.60
15		1.50	1.01
Z1		22.6	27.71
P25 I a	dust	34.23	62.64
P 25 I b		38.58	51.21
11 A		44.56	60.69
1b/z	slag	1.85	2.07
2B		4.23	5.05
2C		4.47	4.89

2.7. Procedure for the preparation of test material for the determination of total iron using the titration technique with potassium dichromate(VI)

The placing of a sample (0.5 g) in a beaker was followed by adding hydrochloric acid and heating without letting the mix start boiling. The insoluble residue was filtered with a hard filter and washed with hot hydrochloric acid (aqueous solution, 1/1; V/V) and hot water. The filtrate was concentrated to a volume of approximately 30 cm^3. The filter with the precipitate was transferred to a platinum crucible, dried, carbonised and burned. The residue was wetted with sulphuric acid (aqueous solution, 1/1; V/V). The foregoing was followed by the addition of approximately 20 cm^3 of hydrofluoric acid and heated until the disappearance of sulphuric acid fumes. Next, the residue was fused with potassium disulphate (VI) and dissolved in concentrated hydrochloric acid (50 cm^3). The obtainment of a weakly alkaline reaction necessitated the addition of ammonia. The iron hydroxide precipitate was filtered off. The beaker containing the stock solution was placed under a funnel (fixed above) with the precipitate.

The precipitate was dissolved on a filter by pouring the former with portions of hydrochloric acid. The solution obtained in the above-presented manner was heated. Just before boiling, a few drops of potassium tetraoxomanganate(VII) were added to the solution, which was then concentrated to approximately 30 cm^3. Next, tin(II) chloride solution was added on a drop-by-drop basis until the yellow colour disappeared. Afterwards, the solution was cooled and mercury chloride was added. The mix was then stirred thoroughly and left to settle. Finally, the reduced iron was titrated with potassium dichromate(VI) against sodium diphenylamine sulphonate. The final stage of the titration process was reached when the colour of the solution changed from green to violet. The entire process of analysis was performed using boiled demineralised water. Because of the presence of oxygen, the use of unboiled water carried the risk of oxidation of Fe^{2+} ions present in the solution to Fe^{3+}.

Table 5. Total iron contents in selected certified reference materials determined using the titration and ICP-OES techniques

CRM	Material type	Certified value [% w/w]	Titration		ICP-OES	
			Result [% w/w]	Recovery [%]	Result [% w/w]	Recovery [%]
3.51	Iron ore	67.55	67.45	99	67.32	99
3.55	Iron ore	59.11	59.11	100	58.85	98
3.57	Iron ore	62.79	62.75	99	62.55	99
PI 3.13	Iron ore	55.85	55.85	100	55.75	100
IMZ 3.50	Magnetite	70.20	70.26	100	69.95	99
EURONORM 685-1	Pre-reduced iron ore	91.10	91.17	100	90.57	99
R40	HBI	90.95	90.76	99	90.55	99
S3	Dust	41.07	41.32	100	41.02	100
S1	Dust	20.01	20.11	100	20.16	100
BCS 381	Slag	13.30	13.40	100	13.15	99
E2	Slag	56.40	56.13	99	56.10	98
SH4/5	Slag	23.20	23.32	100	23.08	99

Table 6. Total iron content in waste ferrous materials determined using the titration and ICP-OES techniques

Sample name	Material type	Metallic Fe content [% w/w]	
		Titration	ICP-OES
697/6	sludge	70.02	70.24
2B-16		60.81	61.80
2A-16		73.78	73.01
697/2	scale	69.39	70.18
15		72.12	72.09
Z1		77.77	77.60
P25 I	dust	64.16	64.15
P 25 I		61.64	62.10
11 A		88.38	89.34
1b/z	slag	2.65	2.77
2B		24.71	23.95
2C		27.79	27.22

2.8. Sample preparation for the determination of total iron content using the ICP-OES technique

A sample (0.5 g) was dissolved in concentrated hydrochloric acid (50cm^3). The undissolved residue was filtered through hard filters directly into 200 cm^3 flasks. The filtrate was washed with hot water, transferred to a platinum crucible, dried and calcined in a muffle furnace at a temperature of 750°C. The cooling of the mix was followed by the addition of sodium bicarbonate (0.4 g) and sodium tetraborate (0.8 g) to crucibles. After mixing, the contents of the crucibles were fused for 20 minutes in a muffle furnace at a temperature of 1050°C. After melting, the contents of the crucibles were leached in a mixture of $HCl+H_2O$ (1/1; V/V). The solutions obtained in the process were evaporated to a volume of 50 cm^3 and combined with the filtrate in 200 cm^3 flasks.

2.9. Comparison of the results of the determination of metallic iron obtained using the titration technique and the ICP-OES technique

The results of the total iron determinations obtained using both methods in relation to the certified reference materials are presented in Table 5. Table 6 presents the results of the determinations obtained in relation to the ferrous waste samples.

In relation to the reference materials, both the classical and spectral techniques produced results consistent with the certified values. In both cases, the recovery of analyte was close to 100 % (Tables 5 and 6). The results obtained using the titration method were comparable with those obtained by means of the spectral technique. It was also observed that among the waste materials subjected to the tests, the highest values of total iron were identified in dust samples, where the concentration of analyte reached 90 %. The slags were characterised by the greatest variation in total iron concentration, where the content of the component subjected to determination was restricted within the range of approximately 2.5 % to 28 %. The determination results obtained in relation to the sludge and scale samples were characterised by a relatively narrow range of variation in terms of analyte concentration. The key stage in the titration-based tests was the reduction of iron with tin(II) chloride. The obtainment of proper results required the performance of the hot reduction process, with the lowest possible excess of tin(II) chloride. The addition of a greater quantity of reducing reagent led to the transition of mercury(II), present in the solution, to a metallic form. In the aforesaid case, it was possible to observe the resultant formation of a grey precipitate containing droplets of metallic mercury. As a result, the process of determination had to be repeated. In terms of the ICP-OES technique, the preparation of the test material for the determination of total iron is significantly less laborious, making it possible to obtain test results sooner if compared with the titration method.

2.10. Determination of acid-soluble iron(II) using chromatometric methods

The identification of the possibility of determining acid-soluble iron(II) was performed by means of two titration methods [24, 25], where potassium dichromate(VI) was used as titrant. The methods differed in terms of sample preparation. Available reference publications contained no reports regarding the possibility of determining iron(II) using instrumental techniques.

2.11. Sample preparation procedure for the determination of acid-soluble iron(II)

The test material was dissolved in hydrochloric acid, without air access, for 20 minutes (Fig. 2). Mixtures of sulphuric(VI) and orthophosphoric(V) (7/1.5/1.5; V/V/V) acid were added to the dissolved samples (0.4 g) and the whole was diluted with water to a volume of 300 cm^3. The determination of the iron(II) content was performed using the titration method with a standard volumetric solution of potassium dichromate(VI), using sodium diphenylamine sulphonate as an indicator. The final point of titration was indicated by a change in the solution colour from green to violet.

The detection of the presence of metallic iron in the waste material (chapter 2.9) entailed the investigation concerning the possibility of competing or consecutive reactions taking place during the process. To this end, it was necessary to prepare a series of synthetic samples, based on the IMZ 3.43 certified iron ore reference material with a known (certified) iron(II) content, in which metallic Fe was not present. A portion of metallic iron was introduced into the reference material so that it would constitute 1, 5 and 10 % of the sample weight. The prepared synthetic powder samples were mixed thoroughly and dried at a temperature of 105 °C. The results of the acid-soluble iron(II) determinations based on the titration method in a series of synthetic reference solutions are presented in Table 7.

The determinations involving ore samples with added metallic iron revealed a significant effect of the metallic form of the element on the results obtained in relation to acid-soluble iron(II). An increase in the amount of metallic iron resulted in a disproportionate and random increase in the determined content of iron(II). Probably, the metallic form of iron was transformed into acid-soluble iron(VI) sulphate, determined along with iron(II) present in the solution.

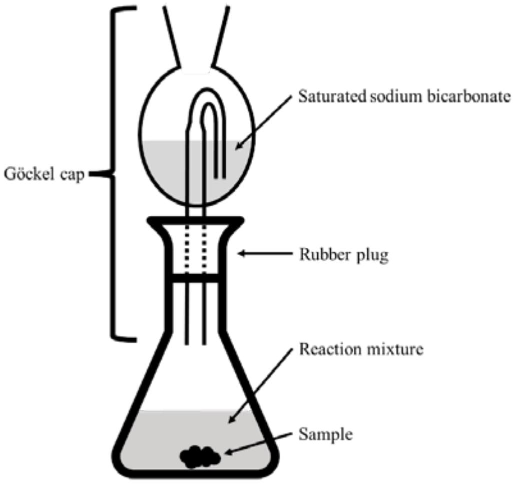

Fig. 2. Flask with the cap used in the determination of Fe(II)

Table 7. Results of the determination of Fe(II) in standard IMZ 3.43 (attested Fe(II) content = 6.37 %)

Sample	IMZ 3.43 without metallic Fe added	IMZ 3.43 + 1% Fe	IMZ 3.43 + 5% Fe	IMZ 3.43 + 10% Fe
Result [% m/m]	6.46	9.05	17.81	25.57

2.12. Sample preparation for the determination of acid-soluble iron(II) in a ferric chloride solution

The placing of the sample (0.5 g) in a conical flask was followed by the addition of a 10 % iron(II) chloride solution (pH 0.95–1.05). The reaction mixture was stirred vigorously for 30 minutes by passing carbon dioxide through the solution (Fig. 3). Afterwards, the solution was filtered. Next, the filtrate with the precipitate was placed in a conical flask and sodium bicarbonate, concentrated hydrochloric acid and sodium fluoride were added. The flask was immediately sealed with a Göckel cap containing a supersaturated solution of sodium bicarbonate. The flask was heated on a hotplate until the sample was completely decomposed. The verification of the correctness of the above-presented sample preparation procedure involved the use of a series of certified reference materials with an attested iron(II) content. (Table 8).

The results obtained in reference materials E2, IMZ 3.53 and IMZ 3.59 deviated significantly from the certified values. However, the results for certified reference materials Euro 685-1, SH 4/5 and IMZ 3.50 were consistent with the certified values.

The reason for the above-named discrepancies could not be established on the basis of the results obtained in the tests. It was not possible to identify any correlation between the overestimation of iron(II) results and the proportion of the remaining forms of iron in the sample. The errors in determining iron(II) in selected reference materials might have originated from secondary chemical reactions taking place during sample preparation. In such processes, part of the iron not originally present in the second oxidation state might have converted to this form, distorting the final determination results.

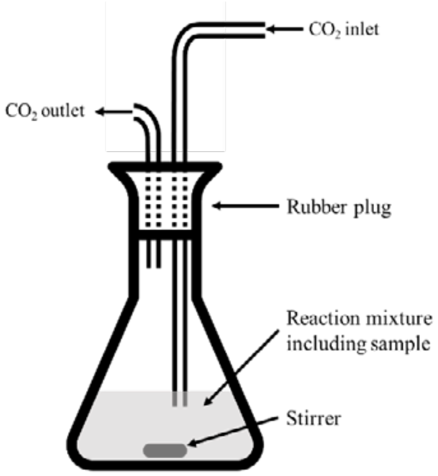

Fig. 3. Set used for the determination of Fe(II) with an addition of iron(III) chloride

3. Conclusions and summary

The tests discussed in the article involved the use of both classical and spectral techniques aimed at identifying the speciation forms of iron in metalliferous waste. The waste material subjected to the tests contained varied amounts of total iron, ranging from a few to over 90 %. The proportions of other forms of iron also varied. The correctness of the adopted analytical procedure was confirmed using certified reference materials and synthetic standards.

The tests revealed that both the classical method and the ICP-OES spectral technique could be used interchangeably for the determination of total iron in waste. However, sample preparation for the determination of total iron using the spectral technique was less complex and time-consuming. The ICP-OES technique was used effectively for the determination of the metallic form of iron. As regards the determination of the metallic form of iron, the results obtained using the titration method were in most cases significantly lower than those obtained using the spectral technique. Such an effect could probably be ascribed to the incomplete transfer of the metallic form of the element into the solution when preparing the sample for titration-method-based determination. A major challenge was the determination of iron in the second oxidation state. The very few subject-related publications have focused primarily on analytes in geology and mineralogy. The issues connected with the identification of this form of iron resulted from its instability in the reaction medium. Iron(II) forms stable solid compounds. During the preparation of samples requiring the dissolution of the sample material, iron(II) could undergo reactions leading to a change in the oxidation state of the element.

In addition, iron(II) in metalliferous waste is usually present along with its other forms which, when affected by the reaction conditions, could be partially converted to the iron form in the second oxidation state. In the course of the aforementioned reactions, the original proportions of the individual forms of iron were disturbed. Consequently, the results of Fe(II) determinations were encumbered with errors. The primary interfering substance identified in the determination of Fe(II) in metalliferous waste was metallic iron.

Table 8. Results of the determination of Fe(II) in certified reference materials, obtained using the chromatometric method after treatment with iron(III) chloride

CRM	Material type	Certified total Fe [% w/w]	Certified FeO [% w/w]	FeO result [% w/w]	Recovery [%]
Euro 685-1	Pre-reduced iron ore	91.10	7.72 (Fe^{++})	8.56 (Fe^{++})	110
SH 4/5	Steel slag	24.10	25.10	25.13	100
E2	Slag	56.40	6.20	10.05	167
IMZ 3.50	Iron ore concentrate / magnetite	70.20	30.06	30.16	100
IMZ 3.53	Iron ore	66.42	1.41	6.46	458
IMZ 3.59	Iron ore pellets	61.74	3.17	10.05	317

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[23] PN-ISO 9035:1999 – Oznaczanie zawartości żelaza(II) rozpuszczalnego w kwasach metodą miareczkową.

[24] Zheng L., Tao J.: Determination of iron (II) in direct reduced iron by iron trichloride decomposition-potassium dichromate titration. Metall. Anal., 2010, no. 2, pp. 65–68.