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Progress and Future of Chemical Analysis Techniques in JFE Group†

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Abstract:

Chemical analysis techniques have played important roles in a diverse range of fields in the steel industry, including product development, stable and efficient operation of manufacturing processes, and preservation of the global environment. This paper reviews the recent status of development of chemical analysis techniques, focusing on the four areas of trace analysis, precipitates and inclusions analysis, online/on-site analysis and organic/environmental/slag analysis.

1. Introduction

More than 10 years have now passed since the JFE Group was created accompanying the merger of Kawasaki Steel Corporation and NKK Corporation. During that period, both steel products and manufacturing processes have become even more advanced. Chemical analysis techniques responding to that progress have supported development in a number of areas, including the development of products and manufacturing processes, stable operation at the manufacturing site and quality control and assurance. Recently, development of chemical analysis techniques has been carried out to address the issue of global environmental conservation surrounding the steel industry. This paper reviews the history of chemical analysis techniques at JFE Steel Corporation to date, and presents an outline of recent trends in techniques in the four areas of trace analysis, precipitates and inclusions analysis, online/on-site analysis and organic/environmental/slag analysis.

In addition, JFE Techno-Research Corporation (JFE-TEC) provides advanced analytical services in which the analytical techniques cultivated in analysis of iron and steel are strengthened in directions aligned with the needs of the world. Therefore, the analytical techniques of JFE-TEC are also introduced.

2. History of Chemical Analysis Techniques

In the period since modern steel manufacturing began, chemical analysis techniques have supported the both manufacturing site and research and development in the steel industry as indispensable basic technologies. At JFE Steel, development of techniques for chemical analysis began around 1960. At that time, when productivity increased dramatically as a result of the introduction of converter steelmaking, the analytical methods that would become main to the steel works also changed greatly, from the wet analysis methods used until then to rapid instrumental analysis methods. Occasioned by this change, the development of rapid analytical techniques became an important challenge for research and development, and even today, steel manufacturers are continuing to promote the development of rapid, highly accurate process analysis techniques. On the other hand, precipitates and inclusions analysis and ultra trace elemental analysis became main analytical techniques for research and development of (steel) product and (steel) manufacturing process. Precipitates and inclusions analysis began in the 1960s, and active research was carried out in tandem with the progress of refining technology from the 1970s through the 1980s. Although wet chemical analysis was the main stream at the beginning, research was also carried out by rapid dry chemical analysis methods from the 1990s. The latter began

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around 1980, and from the 1990s, remarkable progress was achieved thanks to the advent of advanced pretreatment techniques and extremely sensitive analytical instruments, as exemplified by the inductively coupled plasma mass spectrometer (ICP-MS). Tracing back through history, here we will take retrospective view of the chemical analysis techniques developed by JFE Steel, and will introduce those techniques that made important contributions to the development of JFE Steel, and in turn, the steel industry.

In the 1980s, JFE Steel began development of a technique for trace analysis of steel, and established an analytical technique that combined unique analytical operations performed from analysis to measurement of iron and steel specimens at the test tube scale, and matrix separation methods utilizing solvent extraction and chromatography[1–5]. This technique was applicable not only to ferrous materials, but also to other metals, and thus made an important contribution to the development of ultra high purity metals[6]. The usefulness of the developed analytical technique[5] was highly evaluated in many quarters and, for example, received the 1999 the Japan Institute of Metals and Materials Technical Development Award. This technique made a large contribution to materials and R&D.

As representative achievements in the development of analytical techniques for precipitates and inclusions, two techniques developed in the 1980s may be mentioned. P has an extremely high solidification segregation rate in steel, and has a variety of adverse effects on steel products. Therefore, a method for detecting phosphorous segregates was developed as a segregation evaluation method for P[7]. The key points of this method are the corrosion method and coloration method of the surface under examination, which make it possible to evaluate large areas quickly. This method enables simple evaluation of P segregation in steel materials and is particularly effective in evaluations of low-S steels, which had been difficult with the conventional S print method. The second achievement is the alkali fusion-coulometric titration method, which was developed for accurate determination of N as nitride[8]. Because N affects various properties of steel by forming nitrides with Al and Ti, an accurate determination method for N in as nitrides, that is, N in compound form, had been considered necessary. This method was highly evaluated and received the 1989 Best Paper Award from the Iron and Steel Institute of Japan (ISIJ).

JFE Steel also developed outstanding technologies for process control analysis. In the 1980s, a method utilizing the Compton scattered X-ray intensity of the primary X-rays of the X-ray fluorescence spectrometer, which is used in process control analysis of coating layers, etc., was developed as a rapid and highly accurate new coating thickness measurement method with a wide range of applicability[9]. This technology enables rapid, simple measurement of coating thickness, which is a key control item for quality assurance. In the 1990s, JFE developed a laser ablation the inductively coupled plasma atomic emission spectrometer (LA-ICP-AES) method[10] as a rapid analytical alternative to the conventional solid-state emission method, and applied it practically in on-site analysis of slabs[11] and rapid inspection of surface defects of steel products in cold-rolled steel sheets[12], as well as in automatic analysis systems for products[13], etc. The coating thickness measurement method using Compton scattered X-rays and the ICP-AES method won the Best Paper Award of the ISIJ in 1989 and 1998, respectively, and the latter also received the prestigious Okochi Prize for 1997, indicating the high evaluation of this technology.

3. Recent Chemical Analysis Techniques

3.1 Trace Analysis

High purification of iron, and investigation of the fundamental nature of the mechanism by which iron manifests properties when various elements are added, is increasingly important for obtaining high functions in iron and steel materials. Research has revealed that high purity iron has properties that were unknown until now. For example, high purity iron is extremely rust-resistant, and has remarkably high ductility even at low temperatures. Moreover, the ongoing evolution of steel manufacturing processes and higher product needs also requires an action in the development of analytical techniques. From an early date, JFE Steel grappled with the establishment of pretreatment technologies and development of analysis methods applying ICP-AES and ICP-MS, which enable simultaneous analysis of multiple elements, for analysis of trace elements in steel. In particular, in ultra trace analytical techniques combining a sample pretreatment method, which utilizes the solvent extraction method or chromatography, and ICP-MS, determination of many elements at the $\mu g \cdot g^{-1}$ level or lower has become possible[14,15]. The limit of determination of trace elements in iron and steel by methods developed by JFE Steel is shown in **Fig. 1**. Determination at $\mu g \cdot g^{-1}$ or below has been achieved with many elements. Although not shown in the figure, JFE Steel has also developed sub-$\mu g \cdot g^{-1}$ analysis methods for halogen series elements and C, N, O and other gas-forming elements.

As a result of technical innovations in hot metal pretreatment, refining methods, etc. in the steelmaking process, level of high cleanliness of steel has progressed. In particular, S, which has harmful effects on welding,

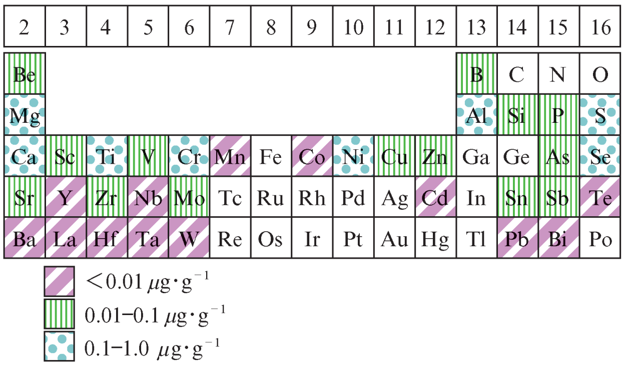

Fig. 1 Limit of determination of trace elements in iron and steel by JFE Steel methods

formability and other properties has been reduced to the $\mu g \cdot g^{-1}$ level. Because the lower limit of application of S analysis in steel by the conventional JIS method is 5 $\mu g \cdot g^{-1}$ [16], it is not possible to respond to the above-mentioned needs. Focusing on the fluorescence method, which has higher sensitivity than the infrared absorption method conventionally used as a S detection method, JFE Steel developed a new method (post-combustion ultraviolet fluorescence spectroscopy) for determination of trace amounts of S in steel with the outstanding accuracy shown in **Table 1** by combining the fluorescence method and high-frequency combustion method[17,18]. The limit of determination by the developed method was 0.5 $\mu g \cdot g^{-1}$, which is one order of magnitude superior to that of the conventional method. Long-term operation tests were performed in the steel works, confirming that this technology has satisfactory stability as a process control analysis device. The newly-developed post-combustion ultraviolet fluorescence spectroscopy method is also superior to the existing method from the viewpoints of analytical accuracy and maintainability, as it is not affected by moisture.

Accurate determination of scarce samples and minute samples is difficult because it is not possible to secure a sufficient amount of the sample material. The direct injection nebulizer (DIN) is a nebulizer for use with ICP-MS/AES which sprays the sample solution directly into the argon plasma rather than introducing the solution via a spray chamber. Because the full amount of the sample can be introduced into the plasma, ionization efficiency and detection efficiency are improved, and trace analysis is possible even with only a small amount of sample material. JFE Steel optimized the conditions of analysis by ICP-MS equipped with this DIN, and established an analysis and evaluation technique for the segregated phase of micro region line defects in cold-rolled steel sheets[19].

JFE-TEC has installed three types of ICP-MS (quadrupole type, double focusing type and triple quadrupole type) in a cleanroom, and performs all processes from specimen pretreatment to measurement in a clean environment. By selecting the optimum instrument and conditions for the sample material, JFE-TEC provides trace analysis at the sub-$\mu g \cdot g^{-1}$ level in materials, beginning with iron and steel, and centering on nonferrous metals, electronic materials, medical materials, etc. In October 2015, the company expanded its cleanroom facilities to include a cleanroom equipped with clean ashing process equipment, creating a system that can provide ultra trace analysis data on electrolyte membranes, catalysts, resists and other polymer materials, and biological and medical and pharmaceutical materials, etc. with even higher accuracy and speed.

Table 1 Repeatability error of analytical results of S in certified reference materials (CRMs) by ultraviolet (UV) fluorescence and conventional infrared (IR) absorption method[17]

Sample	Cert. value ($\mu g \cdot g^{-1}$)	Repeatability error (n10), $\mu g \cdot g^{-1}$	
		UV Fluorescence	IR Absorption
Blank	—	0.05	0.24
JSS001-6	1.5	0.04	0.26
SRM131g	4.255	0.04	0.41
JSS653-14	9.4	0.16	0.55
JSS652-14	13.5	0.07	0.52
JSS244-9	20	0.07	0.52

JSS: Japanese Iron and Steel Certified Reference Material
SRM: Standard Reference Material

3.2 Precipitates and Inclusions Analytical Techniques

Inclusions and precipitates in steel have a large effect on the properties of the steel. For example, because inclusions such as oxides and sulfides have a harmful effect on ductility, toughness and other properties of steel, efforts are made to reduce these inclusions by various refining processes. On the other hand, as useful microstructural components, carbides, nitrides and other precipitates has been studied with the aim of improving material properties, for example, by precipitation hardening, microstructural refinement, etc[20]. Thus, evaluation methods for precipitates and inclusions in iron and steel products are important as technologies supporting both manufacturing processes and material development.

Inclusions such as slag inclusions and powder inclusions, which originate from accidental entrainment in refining processes, consist mainly of CaO and are often chemically unstable. The fact that they dissolve in the extraction process in oxide extraction methods such as acid dissolution methods and the halogen-methanol method, etc. was a problem. Although it was thought that CaO type inclusions could be extracted and separated by an electrolytic extraction method employing a non-aqueous electrolyte, it was not possible to obtain adequate representativeness in evaluation of accidentally-entrained inclusions because the steel sample that could be electrolyzed was small, being only a few grams. Therefore, JFE Steel developed a new non-aqueous electrolyte (40 mass% maleic anhydride-3 mass% tetramethyl ammonium chloride-methanol)[21,22]. This electrolyte enables inclusion evaluation with good representativeness, as CaO type inclusions can be extracted stably, and 100 g of the Fe matrix can be dissolved with 1 *l* of the electrolyte. This method has been utilized in the development of various processes, such as evaluation of casting conditions, evaluation of mold powder entrainment, etc[23].

In recent years, remarkable progress has been achieved in technologies for improving the properties of steel materials by utilizing precipitates, and accompanying this, control of precipitates in manufacturing processes has become important[24]. In precipitation hardened high strength steel sheets, high strength has been realized by precipitates. However, the precipitates contained in steel sheets have been refined to the nanometer level in recent years. Although techniques for accurate quantitative evaluation of these extremely fine precipitates are critical, the analysis values of fine precipitates obtained by the conventional electrolytic extraction method were smaller than the actual amounts. As causes of this problem, precipitates extracted from the Fe matrix by electrolysis were chemically dissolved into the electrolyte or filtration leakage occurred when recovering the precipitates by means of a filter. Therefore, to avoid chemical dissolution of precipitates, JFE Steel developed an electrolyte which stabilizes dissolved iron and reduces the chelating agent that promotes dissolution of precipitates to the limit[25]. As a countermeasure for leakage during recovery with a filter, JFE also developed a simple, fast quantitative analysis method for solid solution elements in steel which does not require a filtering operation[26,27]. As the advantage of this method, solid-liquid separation is carried out by utilizing the fact that the precipitate adheres to the specimen during electrolysis, and quantitative analysis of the solid solution elements dissolved in the electrolyte is then performed after electrolysis. **Figure 2** shows the results of an analysis of solid solution Ti (quantitative analysis for solid solution elements in steel) and precipitated Ti (conventional electrolytic extraction method) in laboratory hot-rolled steel samples that were hot rolled from the same steel ingots. The results for the Ti precipitates in the filtrate that passed through the filter in the conventional method are also shown. It is clear that a larger amount of precipitates passes through the filter as the sample contains finer precipitates, and as a result, the analysis value of precipitated Ti by the conventional

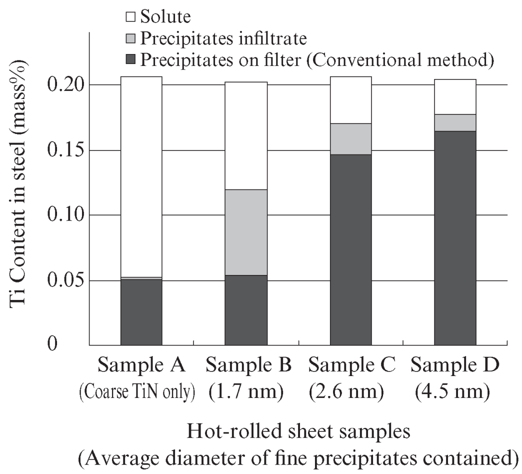

Fig. 2 Analytical results classified by form of Ti in steel sheet samples hot-rolled under different temperature[26]

method is low. Therefore, a simple, accurate evaluation of the amount of precipitated Ti was possible by subtracting the Ti analysis value by quantitative analysis for solid solution elements from the total Ti analysis value, based on the fact that the total of the analysis values is equal to the Ti content (0.20 mass%). As methods for determination of precipitates by size by dispersing the precipitates in an aqueous dispersion medium, JFE Steel developed a method which combines electrospray (ES) and the differential mobility analyzer (DMA)[28,29], and a method for estimation from the relationship between the electrolytic amount and the filtration recovery amount when the electrolytic amount is changed[30]. These methods have made important contributions to the development of steel products at JFE Steel.

Because the chemical properties of intermetallic compounds that precipitate in stainless steel and other high alloy steels resemble those of the matrix and other precipitates, chemical separation and extraction of intermetallic compounds is often difficult. However, there is a strong need for quantitative analysis of the content of intermetallic compounds in these steels, as this influences their mechanical properties. Therefore, focusing on the difference in the chemical dissolution behaviors of precipitates in ferritic stainless steel, JFE Steel established a quantitative analysis by form which is applicable to the Laves phase intermetallic compound[31]. As a distinctive feature of this method, the Laves phase is separated from other precipitates and quantified by selectively dissolving only the Laves phase from precipitates including the Laves phase, which were extracted by electrolytic extraction, by dissolution in a 1 mass% $KMnO_4$ aqueous solution as a secondary treatment. The precipitation behavior of the Laves phase under various stainless steel aging treatment conditions was clarified by using this method[32].

3.3 Online/On-site Analytical Techniques

The role of analytical techniques in iron and steel manufacturing processes is to feedback accurate analytical values to the manufacturing site as quickly as possible. Therefore, in its research and development activities, JFE Steel places strong particular emphasis on rapid analytical techniques.

In the steelmaking process, JFE Steel is promoting the development of online/on-site analytical methods using lasers under severe environments. As a result of these efforts, JFE established an online analytical technique for C in steel which enables rapid analysis with the same accuracy as conventional spark optical emission spectrometry (Spark OES) by a double pulse method which enhances emission intensity by irradiating the specimen at intervals of several microseconds with two laser pulses utilizing LIBS (laser induced breakdown spectroscopy)[33]. Because LIBS has a simple device composition in comparison with Spark OES and requires almost no specimen preparation, a space-saving on-site device which also includes the pretreatment equipment could be realized by the establishment of appropriate laser irradiation conditions. JFE Steel also developed an online analytical technique for Mn in molten steel by atomic absorption spectrometry[34]. This analytical technique focuses on the relationship between the amount of evaporated Mn and the Mn concentration in molten steel, utilizing atomic absorption spectrometry to measure evaporation of manganese atoms from molten steel. As a feature, it uses a highly accurate atomic absorption method in which the influence of fluctuations in the atomization temperature is minimal in comparison with OES. Previous to the development of this JFE technology, there were virtually no examples in which atomic absorption spectrometry was studied as an online/on-site analytical technique due to the high difficulty of the atomization method and light input/output and the low dynamic range of the method. As a result of repeated technical development efforts, JFE Steel solved problems such as utilization of naturally-evaporated atoms, a higher luminescence laser light source, construction of a stable optical system by molten steel surface light reflection, and expansion of the dynamic range by applying a variable wavelength laser, and succeeded in establishing an analytical technique for Mn in molten steel by atomic absorption spectrometry, as shown in **Fig. 3**[35,36].

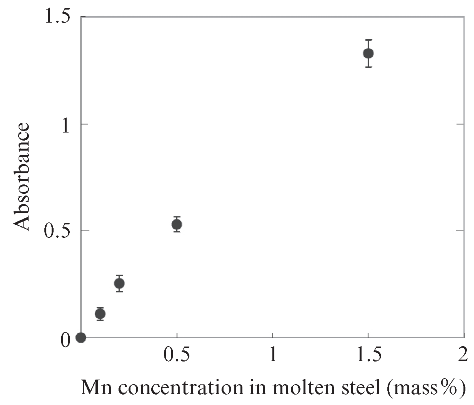

Fig. 3 Relationship between Mn concentration in molten steel and Mn absorbance[35]

Since the concentration of Cr, which is a main element in stainless steel, largely controls the properties of products, the concentration of Cr is strictly controlled. Although Cr had been measured by X-ray fluorescence spectroscopy, which easily secures analytical accuracy, analysis time was long and analytical values were influenced by the polishing roughness of the specimen surface. To solve these problems, JFE Steel established a Spark OES analytical technique in which the metal microstructure at the analysis position is controlled by water-cooling specimens sampled from molten steel, enabling rapid, highly accurate analysis[37].

JFE Steel is also engaged in the development of online/on-site analytical techniques contributing to stable manufacturing of products. In sheet manufacturing processes, the oxide layer that forms on the steel sheet surface is removed by pickling. Control of the concentration of the pickling solution is extremely important for stabilization of product quality because the concentration of the solution changes with use. Due to the increased speed of the pickling line in recent years, the tendency toward large changes in the concentration of the pickling solution in a short time has become stronger. With concentration control by the conventional chemical analysis method, judgment of the results required time, and there was concern that nonconforming products might be produced because the acid concentration could not be adjusted in time. Therefore, JFE Steel established a high speed acid concentration analysis technique by using near-infrared spectroscopy[38–40]. Because use of this analysis method makes it possible to obtain the concentrations of multiple components both rapidly and simultaneously, strict concentration control of pickling processes is expected to be possible. For surface treatment processes, JFE Steel established a simple analytical technique which enables on-site quantitative analysis of the wax coated on steel strips[41].

JFE-TEC provides an on-site analysis service called “GREENFACT®” with a metal material analysis device utilizing a portable Spark OES system[42]. This nondestructive technology makes it possible to perform measurements of the determination of type of steel and different materials in the short time of about 1 min, and is applicable to a full range of measurement object, from small component parts such as motors and bolts to large-scale structures.

3.4 Organic/Environmental/Slag Analytical Techniques

The environment surrounding the iron and steel industry has changed greatly in the past 10 years. Concern about depletion of high quality natural resources, mainly iron ore and coal, and sharp increases in raw material prices are prime examples of this. Under these conditions, JFE Steel has grappled with analysis of raw materials, beginning with coal, for production of coke with high quality and high efficiency. In research on the permeation distance phenomenon, which is one property of coal that was revealed to be a factor in coal strength in recent years, JFE Steel clarified the properties and influencing factors of permeating substances by utilizing gas chromatograph mass spectrometry and Raman spectroscopy[43,44]. JFE researchers also discovered that the thermal history of coal near the softening and melting temperature, of 300–600°C displays a correlation with the property values obtained by Raman spectroscopy measurements[45]. Considering reforming and effective utilization of low grade coals, the effects of addition of various substances on coal viscosity were evaluated[46]. Raw material evaluation and analysis techniques will almost certainly be ever more important for responding to future changes in the grade of raw materials.

The increase in environmental awareness in recent years is also remarkable. The environmental control substances in a steel works include benzene and dioxins. Although the environmental standard for benzene has been set at an annual average value of 3 $\mu g \cdot m^{-3}$, direct analysis of benzene at this level is difficult. Therefore, JFE Steel developed an analytical method for trace amounts of benzene in the atmosphere by atmospheric pressure chemical ionization mass spectrometry (APCI-MS), in which the specimen can be introduced under atmospheric pressure and high ionization efficiency can be expected, and achieved an advanced level of steel works environmental control technology[47].

Measurements of dioxins and other environmental pollutants are extremely labor-and time-intensive. Therefore, as rapid, simple analytical techniques for dioxins, JFE-TEC discovered an indicator substance measurement method with a high correlation with the concentration of dioxins, and an immunoassay method using the antigen-antibody reaction, and established rapid analysis methods for the dioxin concentration[48–52]. In addition to these simple methods, JFE-TEC is currently working to achieve automation and higher speed in the processes of official analytical methods, and has realized reporting of results within 3 days as the shortest reporting period.

Iron and steel slag, which are byproducts of the steel manufacturing process, are used as basic materials for social infrastructure in the forms of cement and concrete aggregate, roadbed materials, etc. based on appropriate consideration of the swelling behavior of the slag. The main cause of slag swelling is hydration of substances such as free calcium oxide (free-CaO), free magnesium oxide (free-MgO) and the like. In order to understand slag swelling behavior, it is important to quantify the free-CaO and free-MgO contents in the slag. Although the ethylene glycol (EG) extraction method is widely used in determinations of free-CaO in slag, the problems with this method included the fact that the dissolution behavior of Ca compounds other than CaO in EG was not clear, and there were large variations in the analytical values. Therefore, JFE Steel carried out a new study of the EG method and clarified the factors causing changes in analysis values in Ca analyses of Ca compounds and free-CaO[53]. Furthermore, the company also found that I_2-alcohol-EG is an effective solution for dissolution of the free-MgO and $Mg(OH)_2$ in slag, and established a method for determination of free-MgO in slag by combined use of I_2-alcohol-EG and thermogravimetry[54–56].

Stabilization of slag quality and higher added value of slag products are expected in order to promote and expand the use of iron and steel slag. With the aims of higher added value and reforming of slag, JFE Steel created a prototype of a hydrothermal treatment device for iron and steel slag by high temperature, high pressure water[57]. As a result, it was found that the reactivity of the treatment water increases and the most effective hydrothermal treatment is possible at 250°C, at which the ion product of water reaches its maximum. This hydrothermal treatment was found to be effective for elution of the S component from steelmaking slag and air-cooled blast furnace slag[57,58]. Slag treatment using high temperature, high pressure water is expected to be applicable not only to slag reforming, but also as an accelerated test under aging conditions. In addition to chemical evaluations, safety evaluations of slag are also performed from the biological viewpoint[59].

In the future, JFE Steel intends to deepen its analytical techniques through analysis and evaluation not only of iron and steel products, but also of raw materials, byproducts, environmental control substances, etc.

4. Future Outlook

An outline of the history and recent progress of analytical techniques in the JFE Group was presented. Analytical techniques have progressed accompanying higher added value in products and the evolution of manufacturing processes. In the future, efforts to develop new analytical techniques that provide even higher speed and accuracy will be necessary. In particular, stronger demands for rapid analytical techniques for manufacturing processes and increasingly high needs for online/on-site analytical techniques are likely. Solutions to the question of how to perform stable analysis under the severe environments of production sites will be urgently needed.

With higher functionality of iron and steel products and technical development of steel manufacturing processes, technologies for controlling trace elements in steel and correct, high accuracy analytical techniques for those elements will become critical. In particular, wet chemical analysis, including analysis of trace elements, is the standard for all analytical techniques. It appears that the importance of those techniques will be recognized anew. Although a decrease in the numbers of experienced technicians in the field of wet chemical analysis is a concern, the skills of these techniques must be passed on surely to the next generations in order to support iron and steel processes and research and development. Moreover, for further technical development, active introduction of both leading-edge analytical techniques and techniques used in other fields will be necessary.

The areas related to analytical techniques in the steel industry span a wide range. As described up to this point, analytical techniques are necessary in every situation from research and development to the production site, and from raw materials not only to products, but also to byproducts, and the basic philosophy of these techniques is rapid feedback or feed-forward of accurate values. That has not changed in the past or the present, and will undoubtedly remain unchanged in the future as well. The JFE Group will continue its untiring efforts for the next 10 years of analytical techniques, aiming to maintain and improve the world's most advanced analytical techniques.

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