AN EVALUATION OF SAMPLING TECHNIQUES FOR THE EMISSION SPECTROCHEMICAL ANALYSIS OF CAST IRON

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by

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A Thesis Submitted to the Faculty of Graduate Studies and Research in Partial Fulfilment of the Requirements for the Degree of Master of Engineering

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TO MY FRIEND ANNE COWLING

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ABSTRACT

Seven different molds, which are in common use by cast-iron foundries in North America, were evaluated for both their convenience of use, and for the repeatabilities of the chemical analysis of their samples, by vacuum-emission spectrometry. The elements analyzed were carbon, manganese, phosphorus, sulfur, silicon, copper, and magnesium. Four types of cast iron were investigated - white, gray, nodular, and corrosion-resisting austenitic.

The precision of the spectrochemical analysis was found to be related to the microstructure of the sample. Small additions of a carbide stabilizer (e.g. 0.05% Sn or 0.08% Bi) to the melt in the sampling spoon resulted in complete chilling of the samples, and improved the precision of the spectrochemical analysis of carbon by a factor of 5 to 12. The results of the spectrochemical analysis were statistically analyzed at 4 degrees of freedom and the 99% significance level. Sept différents moules, qui sont communément employés dans les fonderies de fonte en Amérique du Nord ont été évalués pour leur commodité ainsi que pour l'uniformité des analyses chimiques, par spectromètre émission sous yide, de leurs échantillons pour les suivants: carbone, manganèse, phosphore, soufre, silice, cuivre et magnèsium. Quatre types de fonte ont été évalués: la fonte blanche, grise, nodulaire et austenitique résistant à la corrosion.

RESUME

Il a été trouvé que la précision de l'analyse spectrochimique est reliée à la microstructure. De petites additions de carbures stabilisateurs (i.e. 0.05% Sn ou 0.08% Bi) au métal en fusion dans la cuillière d'échantillormage ont résulté en un refroidissement complet des échantillons et en une amélioration de la précision de l'analyse spectrochimique du carbone, de l'ordre de 5 à 12. Les résultats de l'analyse spectrochimique ont été analysés statistiquement, à 4 degrés de liberté et 99% niveau de signification.

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CHAPTER 1 LITERATURE REVIEW

1.1 INTRODUCTION

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The achievement of rapid and accurate chemical analysis of cast iron melts is an important aspect of the foundry industry. Fast chemical analysis shortens the ladle- and furnace-hold time and, consequently, increases the production rate at minimum running costs. Accurate chemical analysis helps in making heats of the required chemical compositions, thus minimizing the amount of in-house scrap.

The use of direct-reading spectrometers for the control of metal composition has extended in scope, from its beginnings in the late 1940s for the analysis of aluminum and its alloys, to cover the whole of the requirements of the ferrous and non-ferrous industries.⁽¹⁾ The most advanced practice involves computers in vacuum-emission spectrochemical analysis. This useful advancement makes it possible to obtain a direct reading of the chemical composition of an analyzed sample in as short a period as 2 or 3 minutes, as well as quick and easy standardization of the apparatus.

There are, however, certain problems in analyzing cast-iron melts. Chief among these problems is achieving the maximum accuracy of the chemical analysis when using the most convenient sampling mold. The common sampling molds, used by foundrymen, can give different microstructures for a given cast-iron melt. This thesis is concerned with evaluating the common sampling molds for the spectrochemical analysis of different cast-iron melts and relating the analytical behavior to the microstructure of the analyzed sample. Hence, a good understanding of cast-iron metallurgy is important, and the next section deals with the solidification of cast irons.

1.2 SOLIDIFICATION OF CAST IRONS

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1.2.1 Equilibrium Phase Diagram

Iron-carbon alloys may solidify with the carbon present as either graphite or iron carbide. Graphite is the thermodynamically stable phase but, for kinetic reasons, iron carbide often forms. Thus, the iron carbide phase diagram, as shown in Figure (1-1), can be represented as two superimposed phases diagram, one for Fe-C (the stable system) and the other for Fe-Fe₃C (the metastable system). This combined diagram can be used to interpret cast iron structures under different solidification conditions. The interpretation of the structures of cast iron is complicated because in many cases solidification takes place according to the stable system, whereas subsequent transformation in the solid state takes place according to the metastable system. In addition, the structures of cast irons are greatly influenced by the undercooling of the melt, ⁽³⁾ which is promoted by both melt-superheat and alloy addition.

Eutectic solidification begins from a number of centres or nuclei and consists of a decomposition of the liquid into austenite and graphite for the stable system, and into iron carbide and austenite for the metastable system of hypoeutectic cast irons. On the other hand, hypereutectic cast irons start to solidify by the decomposition

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FIGURE (1-1) Iron-carbon "double diagram" for cast iron.⁽²⁾

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of the liquid into iron carbide for the metastable system, and into graphite for the stable system. The generally prevailing opinion is that this graphite nucleates on heterogeneous substrates in the liquid. $^{(4,5,6)}$ In addition, graphite has been considered to form either by decomposition of the carbide phase formed on solidification, $^{(7,8)}$ or by precipitation from supersaturated austenite. $^{(9,10)}$

There is no doubt that alloying elements influence the structures of cast irons. Elements like silicon, nickel and copper promote the formation of graphite by decreasing the stability of cementite. ⁽³⁾ Silicon significantly alters the eutectic composition, as well as the maximum solubility of carbon in austenite. As shown in Figure (1-2), as the silicon content increases, the maximum solubility of carbon in austenite decreases ^(11,12) from E to $E_1 - E_4$. Therefore, silicon helps form free graphite by precipitation from supersaturated austenite. On the other hand, a carbide stabilizer, such as magnesium, has an adverse effect when it is added to the iron melt, ⁽¹³⁾ as shown by moving point . E to E_{II} . It may also be noted that the introduction of silicon into the system raises the temperature of the eutectic reaction.

1.2.2 Solidification of White Cast Iron

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The suppression of the eutectic transformation in the stable Fe-C system by increasing the degree of undercooling results in an increasing probability for the nucleation of cementite instead of graphite. Once nucleated, cementite growth is much faster than graphite and dominates the solidification process.⁽¹⁴⁾ Detailed studies of nucleation and growth of the white iron eutectic have revealed that

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Compilation of several Fe-C-Si diagrams. The Fe-C diagram is plotted as a function of the Si content; 0%, 1%, 2%, 3% and 4% Si.(11,12)



(CE), wt.%

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cementite has a strong tendency to form two-dimensional dendrites which grow with maximum speed in an edgewise direction; (15) that is, in the direction of the a and b axes of the orthorhombic lattice.

The solidification of hypoeutectic white iron usually proceeds by the following sequence: (15)

a) nucleation and growth of proeutectic austenite dendrites,

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- b) nucleation and growth of clusters of cementite plates;
- c) nucleation of secondary austenite on the cementite plates, and

d) cooperative sidewise growth of cementite and austenite. The structure which grows is illustrated in Figure (1-3).

In spite of the fact that only the sidewise growth resembles a true cooperative process, the edgewise growth of cementite is more rapid. Controlled solidification experiments have shown that the edgewise growth occurs in the direction of a steep temperature gradient and the resultant microstructure resembles the regular lamellar structure typical of cooperative growth. ⁽¹⁶⁾ Figure (1-4) shows a typical structure of white-iron eutectic when formed during controlled solidification.

1.2.3 . Solidification of Gray Cast Iron

In iron-carbon silicon melts, solidification usually starts by nucleation and subsequent growth of the proeutectic constituent (austenite in hypoeutectic irons or kish graphite in hypereutectic iron). Nucleation begins and growth continues from the liquidus temperature down to the eutectic start temperature. The eutectic melt solidifies FIGURE (1-3) Schematic illustration of eutectic growth in the Fe-Fe₃C system. White phase is cementite; black phase is austenite.(16)

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Edgewise growth Cementite is leading

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Crystallographic c-direction of cementite_____

Sidewise growth

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Cooperation is important

FIGURE (1-4) Structure of white iron eutectic when formed during controlled solidification, X60. The etchant was not reported. (16)

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next, as a combined growth of the austenite and graphite phases. The eutectic growth begins from nucleation centres or substrates. In this case, the graphite precipitates within so-called eutectic cells in the form of branched flakes, (16) as shown in Figure (1-5). Figure (1-6) shows a photomicrograph of gray cast

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The flake graphite in cast iron can assume a considerable variety of structures representing different degrees of dispersion. ^(4,18) Examples of such degrees of dispersion are shown in Figure (1-7). The dispersion of the graphite in a eutectic cell depends upon the rate of solidification, which is related to the degree of undercooling. ⁽¹⁹⁾ In many cases, coarse and fine graphite grow side by side, as shown in Figure (1-8).

Apart from the rate of solidification, the growth of graphite is greatly influenced by alloying and impurity elements. Among these is sulphur, which increases the activity of carbon in the melt and decreases its solubility. Therefore, the growth of graphite is promoted by an increase in the sulphur content in the cast iron melt.⁽²¹⁾ Also, when the sulphur level in the melt increases, the degree of constitutional undercooling increases,⁽²²⁾ and this in turn increases both the nucleation rate of iron-graphite eutectic cells,⁽¹⁸⁾ as well as their number. These effects of sulphur on the solidification of gray cast iron are shown in Figures (1-9) and (1-10). Very high sulphur contents generate high degrees of undercooling, and cause the graphite eutectic to be replaced by the carbide eutectic. Thus, sulphur may have a graphitizing effect at very low levels, but a carbide-promoting effect at high levels.⁽²¹⁾

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FIGURE (1-6) Pearlitic gray cast iron. Etched in 5% nital, X900.(17)

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FIGURE (1-7) Different degrees of dispersion of free graphite. (18)

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- uniform distribution, random A: orientation
- B:
- C:
- rosette groupings superimposed flake sizes, random orientation interdendritic segregation, random orientation D:
- E: interdendritic segregation, preferred orientation





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FIGURE (1-9) Effect of sulphur content on undercooling. ⁽²¹⁾ The gray cast iron was cast in round bars of 1.2 in in diameter.

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FIGURE (1-10) Influence of sulphur on the Fe graphite eutectic cell number. ⁽²¹⁾ The gray cast iron was cast in round bars of 1.2 in. in diameter.



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The number of graphite-eutectic cells depends on the amount of total undercooling, i.e. both the constitutional and the thermal. Thermal undercooling is a function of the amount of superheat and the cooling rate. The presence of carbide stabilizers (e.g. Mn, Mg or Ti), which neutralize sulphur by desulphurization in the cast iron melts, lowers the constitutional supercooling. Therefore, there is no arbitrary upper limit for sulphur to act as a graphitizer in cast iron melts.

1.2.4 Solidification of Ductile Cast Iron

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The addition of a small amount of magnesium, calcium or cerium to a relatively pure cast iron melt results in nodular rather than flake graphite, and the formation of ductile or nodular cast iron. Figure (1-11) shows a photomicrograph of this material. It has been reported that many elements of the first, second, and third groups in the periodical table, as well as rare earth elements, possess some ability to promote nodule formation, but their effectiveness is limited to high purity melts.⁽²⁴⁾

Nodularizing elements have certain properties in common. They are always in the gaseous state at the temperature of the molten iron, have little solubility in both the iron and the graphite lattice, (25,26) are strong deoxidizers and desulphurizers, and possess the ability to form ionic carbides.

The precipitation of graphite spheroids is always associated with an increased surface tension of the melt. (27,28) This increase is a result of the removal of surface-active elements, especially sulphur and oxygen, from the melt, either through chemical reactions with the

FIGURE (1-11) Ferritic ductile iron, X250. The etchant was not reported.(23)

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nodularizing elements or by treatment under high vacuum. Studies of the relationship between the subversive element content and the surface tension have shown that no spheroids appear below a certain surface tension value. $(^{29}, ^{30})$ Therefore, a high surface tension of the melt seems to be a necessary condition for spheroidal graphite formation.

1.3 PREPARATION OF SAMPLES USED FOR SPECTROCHEMICAL ANALYSIS OF CAST IRON BY VACUUM EMISSION SPECTROMETRY

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Any sample used for spectrochemical analysis by vacuum emission spectrometry must be free from the following defects: ⁽³¹⁾

- Changes in structure which occur when the depth of chill of the sample is not adequate and the analyzed surface is gray. A lack of reproducibility of spectrochemical analysis of carbon is, then, likely to occur.
- 2) Cold laps. There is some reason to believe that, although the discontinuity can be apparently eliminated during grinding, the structure of the sample where the lap occurred may still exhibit segregation of carbides.
- 3) Cracks, porosity and shrinkage defects which are usually visible on the sample surface after preparation. Segregation often occurs around such defects, and this worsens the accuracy of spectrochemical analysis.
- 4) Slag inclusions. Slag usually contains magnesium and manganese sulphides and silica. Thus, analysis of surfaces which are not free of these inclusions results in erratic chemical analyses of magnesium, manganese, and silicon.

Thus, the ideal sample for spectrochemical analysis must have a clean, sound surface with a white iron structure.

1.4 DEVICES USED FOR MELT SAMPLING IN IRON AND STEEL MAKING

Many devices, which aim at producing ideal samples, are used to sample cast iron and steel melts. Some common examples of these sampling devices will now be described.

1.4.1 Clean Pre-heated Steel or Refractory Spoon

This device is used to sample any lightly slagged melts, such as occur in:

- i) ingot molds
- ii) tundishes

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- iii) iron runners
- iv) foundry ladles
- v) cupolas
- vi) electric furnaces
- vii) induction furnaces

The sampling spoon is used to cast wires of 3-5 mm diameter (for carbon- and sulphur-chemical analysis on induction furnaces) and to fill the sampling molds for chemical analysis on vacuum emission spectrometers.

1.4.2 Automatic Device to Sample the Melt during the Blow of Oxygen Furnaces

This device consists of two molds (or two pots) which are some 30 cm apart vertically, to enable studying the homogeneity of the melt bath. $(^{32)}$ The molds are fastened to a steel bar 4 m long which is connected to a lowering cable wound on a drum. The arrangement of the molds alongside the steel bar is shown in Figure (1-12). The sampling bar is made of standard grade steel, the diameter being 30 mm. The connection of the steel bar to the steel cable is through a hook which allows rapid and uncomplicated bar replacement between two sampling actions. This point is important because the bar emerges covered with metal and slag and cannot be employed for the next sampling action. The molds are capped with pressed steel covers which do not melt while passing through the slag, but do melt in the bath, thus minimizing contamination of the sampled melt by slag.

1.4.3 Chilled Sucker Sampler

Use of the chilled sucker sampler to sample the melt bath minimizes the loss of alloying elements that are easily oxidized, e.g. Mn, Si and Mg. It has been shown that manganese oxidizes while in the sampling spoon, resulting in low analysis for this element.⁽³⁴⁾ Figure (1-13) shows the chilled sucker sampler. It consists of 3/8" I.D. galvanized pipe with a pump threaded to one end and the chilled mold to the other end. A sucker cartridge is placed over the assembled mold unit, and a piston on the top of the pump is depressed against the floor to cock the sucker sampler pump. A quartz snorkel tube

FIGURE (1-12) Detail of the sampling bar; disposition of the pots.⁽³³⁾

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FIGURE (1-13) Schematic design of a chilled sucker sampler. (35)

1:	piston
2:	pump
3:	3/8" I.D. galvanized pipe
4:	disassembled chilled mold
5:	disposable sucker cartridge
6:	paper tube
7:	afartz snorkel tube

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attached to the end of the sucker cartridge is positioned over the melt to be sampled and immersed smoothly and immediately to a depth of 5-7 cm. The pump trigger is then pulled and the immersion is continued to the upper end of the small paper tube, which holds the quartz snorkel tube. After the cartridge and the mold are removed, the mold is tapped with a rubber hammer and the sample ready for vacuum emission spectrochemical anælysis is removed.

The chilled sucker samplers have the following advantages: (35).

- Minimal losses of alloying elements, since no spoons or sampling molds are used.
- 2) The ability to sample melts of any fluidity, since the melt-flow to the mold cavity is due to metalostatic pressure and pumping action.

3) The samples are chilled, i.e. free of graphite. Nevertheless, the chilled sucker samplers do possess some disadvantages, such as:

- The molds are not disposable, and contamination from previous heats cannot be avoided entirely, even though careful attention is paid to cleaning the mold between heats.
- 2) The molds cannot be used to sample heavily slagged melts, since the design of the sampler does not prevent slag-flow to the mold cavity through the quartz snorkel tube.

The use of lollypop samplers overcomes the disadvantages of the chilled sucker samplers.

1.4.4 · Lollypop Sampler

The lollypop sampler has the same advantages as the chilled sucker sampler; however, it does not possess the disadvantages of the latter. Figure (1-14) shows the design of a lollypop sampler. When the sample is taken, the protective cap keeps surface kish or slag from entering the lollypop sampler. The control fuse provides a slight time delay for temperature equilibrium and contains a carbide stabilizer to treat the sampled melt, so that the sample is completely chilled. Usually, the control fuse is made of aluminum, but its material composition varies according to the type of melt, the temperature of the melt and the depth of the slag. (36)

The control chamber receives a determined amount of the melt, thereby initiating treatment of the sample. The treated melt then enters the mixing chamber through an off-centered hole, which induces a vortex or turbulence. This results in a homogeneous mix, which then flows into the specimen mold where it is solidified.

The steel pipe is bent to provide a stopper to the sampler at a certain depth and to ensure a certain inclination angle of immersion. The immersion is for 5 to 10 seconds, depending upon the type and the temperature of the melt being sampled.

The sample is recovered by breaking the lollypop sampler about 10 cm from the charred end and removing the hot sample with tongs.

1.4.5 Disposable and Permanent Sampling Molds

In addition to the previously described sampling molds, many different disposable and permanent sampling molds are used. Seven-of

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FIGURE (1-14) Schematic diagram of a lollypop sampler. (36)

- 1: protective cap 2: control fuse 3: control chamber 4: mixing chamber 5: test mold 6: cardboard tube 7: 1" steel pipe

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these other types were used in this research. These molds are in common usage by foundrymen in North America, and will be discussed in Chapter 2.

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1.5 VACUUM EMISSION SPECTROMETRY

1.5.1 Instrumentation

The function of the modern direct-reading emission spectrometer is to provide rapid, reproducible, and accurate analysis. The principle of operation has remained unchanged since the introduction of photomultipliers in the late 1940s. These enabled spectroscopists to use electronic methods instead of photographic plates to measure spectral intensities.⁽³⁷⁾

For a better understanding of the operation of these instruments, a brief discussion of the theory of the generation of spectral lines and their path in a spectrometer will be given. Figure (1-5) shows the details of the sample compartment in the spectrometer. The energy required to excite the sample is provided when a continuous high intensity electric discharge or arc passes between the electrode and the sample surface. Before and during the excitation, the excitation gap (the gap between the surface of the sample to be excited and the counterelectrode tip) is flushed with argon in order to sweep the discharge debris and oxygen. Since the analytical wavelengths of carbon, phosphorus and sulphur are in the far ultraviolet region of the spectrum, oxygen absorbs these wavelengths, ⁽³⁹⁾ thus necessitating the argon flush.

According to Bohr, radiation occurs when there is atomic or ionic transition from some discrete higher energy level to a lower one,

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FIGURE (1-15) Sample compartment in vacuum emission spectrometer.⁽³⁸⁾

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i.e. relaxation of an excited atom or ion.400 Prior to radiation, however, the atom should be excited by a definite amount of energy which will cause an electronic transfer from a lower to a higher energy state. However, the excited state is not stable, and the atom has a limited lifetime in the excited state, which is generally shorter than 10^{-8} second. At the end of this lifetime, the excited atom is relaxed by electronic transfer from the higher energy state to the lower one, and atomic radiation is emitted. In a similar way, ionic radiation can be obtained when the energy transferred to the atom during excitation is increased to such a point that an electron is completely removed from the atom to produce a positively charged ion which then relaxes to emit light. Figure (1-16) shows the sequences of the generation of spectral lines.

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When the spectral lines are dispersed either by a prism or a diffraction grating, they emerge as a light spectrum having a pattern determined by the atoms that have been excited. Since atoms of different elements contain different electron configurations, each element has a distinct and characteristic spectrum, with spectral lines occurring at different wavelengths. ⁽⁴¹⁾ Each element can be identified by its characteristic lines; i.e. the specified wavelengths of the atomic and ionic spectral lines.

Line brightness is a function of element concentration in the sample, and hence can be used for quantitative analysis. Line brightness is converted from radiant energy into electric current by a suitable photomultiplier, conventionally called a phototube. The output of the phototube is fed to the read out for storage on a capacitor.⁽⁴²⁾ There



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is a capacitor for each unknown-element phototube and one for the reference element, e.g. Fe in iron base alloys. Figure (1-17) shows the path of spectral line inside a vacuum emission spectrometer. The instrument is called vacuum spectrometer because the exit and entrance slits, diffraction grating and phototubes are maintained in a vacuum chamber.

1.5.2 Analytical Cycle Periods

The analytical cycle of an emission spectrometer consists of three periods: flush, excitation (or pre-integration), and integration. The functions of each are described below.⁽⁴⁴⁾

a) Flush period

After the spectrometer is activated by depressing the start button, the argon flow rate increases from its low standby rate, generally of the order of 0.5 ℓ/\min ,⁽⁴⁵⁾ to a higher rate, ranging from 2-6 ℓ/\min .⁽⁴⁵⁾ This increase in argon flow rate sweeps air from the spark-stand cavity. With air path spectrometers, it was found impossible to analyze for carbon, sulphur and phosphorus, because the only available analytical wavelengths are in the far ultraviolet region of the spectrum (shorter than 2,000 Å ⁽⁴⁶⁾) and the emitted radiation in this region is readily absorbed by oxygen in the atmosphere and in the spectrometer.⁽³⁹⁾

b) Excitation period

The excitation period establishes stable emission characteristics prior to the analysis, by applying the electric discharge between

FIGURE (1-17) The path of spectral line inside a vacuum emission spectrometer.⁽⁴³⁾

1: sample excitation chamber 30.

- entrance mirror 2:
- 3: entrance slit
- 4: drive shaft

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- 5: grating 6: focal curve 7: exit slit
- 8: phototube
- capacitor 9:



the electrode and the sample and maintaining the discharge until the end of this period. During the pre-integration period the flow rate of argon may drop to a value intermediate between the high flush rate and the low standby rate.

c) Integration period

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At the end of the excitation period, the measuring facilities of the instrument are activated by allowing the current produced from the photomultipliers by the light emission to be fed to, and stored by, the integrating capacitors for each element. With conventional instruments, the discharge conditions and the argon flow rate remain the same during both the integration and the excitation periods.

Integration of the amount of current collected by the capacitors builds up a voltage which varies as the element content of the material is analyzed. At the end of the integration period the discharge is switched off and the argon flow rate returns to the standby level. With the help of a digital computer, the voltage is transformed to scalar counts that can be displayed as percent chemical composition.

1.6 AIM OF THIS THESIS

An extensive review of the literature has not revealed any elaborate studies on the precision of vacuum emission spectrochemical analysis of cast iron melts.

The present research was undertaken with the following objectives:

 To evaluate, for various cast irons, several different molds which are in common use by the North American foundry industry.

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- To relate the consistency of spectrochemical analyses to the microstructures of the analyzed samples.
- To improve the repeatabilities (or the precision) of spectrochemical analyses of the cast iron samples.

CHAPTER 2

EXPERIMENTAL PROCEDURE

. . TYPES OF CAST IRONS MADE

White, nodular, gray, and corrosion-resisting austenitic cast irons were made. Table (2-1) lists the nominal compositions of these alloys.

2.2 MATERIALS FOR CHARGE PREPARATION

The materials used for the charge preparation (with their chemical compositions and physical forms) are listed in Table (2-2). The charging sequences of these materials will be discussed in Section 2.3, where the melting practice is dealt with.

2.3 MELTING PRACTICE

2.3.1 Melting Furnace

The melting equipment consisted of a 150 KW, 3 KHz Toco Meltmaster station which powered an inductotherm induction furnace. This induction coil had a capacity for melting approximately 200 lb of iron. The melts were contained either in alumina crucibles (90% Al_20_3) or in high purity magnesia crucibles. The magnesia crucibles were used in the production of ductile cast iron to minimize the fading of magnesium, ⁽⁴⁷⁾ since magnesium reduces the alumina, and consequently can be slagged if alumina crucibles are employed.

INDE	(2-1)	nominai	cast	tron	composition.

	· · ·	- 7 .		Comp	osition,	wt%		-	~
Type of Cast Iron	C	Mn .	Р	S	Si	Cu	Mg	Ni	Cr
white	3.06	0.569	×0.0900	0.0900	0.650	0.1500			- -
nodular	3.20	0.529	0.0208	0.0089	1.875	0.0370	0.0286	-	-
gray	3.12	0.760	0.3700	0.0760	1.653	0.1200	-	-	-
corrosion- resisting austenitic	2.78	0.429	0.0201	0.0230	3.712	7.5000	-	17.5	. 2.5

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Type of Charge Material	Physical Form	С	Mn	Р	S	Si	Mg .	Ni	Ca	Cu
pig iron	pigs	4.33	0:009	0.026	0.006	0.19	₹.	-	-	
steel scrap	punchings	0.01	-		_ ^	-		- -	-	-
Fe-Si alloy	powder	0.06	0.440	0.025	. 0. 020	48.00	-	0.20	0.22	0.26
Fe-Mn alloy	lumps	6.64	75.510	<u>`</u> _	-	0.27	-	-	-	. -
copper	plates	-	-	-	· _		-	- 1	-	99.00
FeS	powder	-	· - ,	-	36	- 1	-		-	-
Fe-P alloy	lumps	, -	-	20	- ```	3.00	-	-	->	<u> </u>
nickel	pellets	-	′ _	-	-)	-	-	99.5		-
Fe-Cr alloy	lumps -	6-7	-	* -	-	3-6-	<u> </u>	-	-	_
Mg-Ni alloy	ingots	2.00	<u> </u>			_	4.5	93.5	-	,

TABLE (2-2) The compositions of the charge materials and their physical forms.

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Control of the power supplied by the melting unit to the induction coil permitted one to obtain the desired melt bath temperature. In the preparation of the melts, 30 to 60 KW of power were used in the induction furnace. This was 20 to 40% of the full power rating of the Toco Meltmaster.

2.3.2 Charging Sequences

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Pig iron, steel scrap, copper, and nickel (if used) were charged together in the furnace at the start of the melting operation. After the basic charge was melted, the furnace power was turned off and the additions of the remaining charges were made to the crucible. Thereafter, the furnace power was turned on to bring the bath temperature to the desired value. To minimize both the fading of free graphite nuclei and nodularizing elements, as well as the high losses of chromium, sampling of the cast-iron melts was done as soon as the melt temperature reached the required value.

The magnesium-nickel alloy used in the production of ductile cast iron was added after the additions of ferrosilicon, ferromanganese, ferrous sulphide, ferrophosphorous, and ferrochromium alloys. This was done because magnesium has the highest losses while in the melt bath. Sampling of the cast iron melts was done from 3 to 7 minutes after, and 1 minute after the addition of the ferrosilicon and magnesium nickel alloys, respectively.

2.3.3 Temperature Control

The melt temperature was measured with an R-type (Pt/Pt-13% Rh) Dip-Tip thermocouple supplied by Leeds & Northrup Canada Ltd. The applicable temperature range of that thermocouple is 0 to 1778° C, with a maximum error of $\pm 1.0^{\circ}$ C. ⁽⁴⁸⁾ The temperature readings were taken at about 2 cm below the bath surface.

In practice, control of the temperature of the melt is very important. Pouring melts of low superheat results in cold shuts. On the other hand, an excessive superheat is a source of high porosity, scabs, and rat tails in the castings, and promotes fading of free graphite nuclei which may exist as undissolved graphite clusters.⁽⁴⁹⁾ Such high superheating helps undissolved graphite clusters to dissolve in the melt.

Normally, the superheat of the cast iron melt is kept in the range of $150-250^{\circ}$ C. This same range of superheat was used in these experiments, and the liquidus temperature of the cast iron alloy was roughly estimated from the Fe-C-Si equilibrium diagram. The sampling temperature of the melt, which is equal to the liquidus temperature plus the amount of superheat, was controlled by the fine adjustment of the melting-unit power within the range of 0.15-0.30 KW. Table (2-3) summarizes the amount of superheat employed in the production of the cast irons. As shown in the table, the amount of superheat lies in the range 160-225°C, which coincides with the applicable range in cast iron foundry practice.

TABLE (2-3) Summary of the amount of superheat and alloy type for the cast irons made.

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	Type of Cast Iron	Liquidus Temperature, o _C (11)	Sampling Temperature, ^O C	Amount of Superheat, OC	A11oy - %C	Eutectic - %C (11)	Kind of Alloy
a)	white	1240.	1400	/ 160	3.06	4.04	hypoeutectic
, b)	nodùlar '	, 1175	1400	225	3.20	3.63	hypoeutectic
ຸ c)	corrosion- résisting aùstenitic	1225	1400	175	2.78	3.20	austenitic
d)	gray	1190	1400	210 ·	3.12	3.71	hypoeutectic

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2.3.4 Effect of Furnace Holding Time on the Fading of Free Graphite Nuclei

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There is always a furnace holding time period between inoculation and teeming (or sampling) of the melt. During that period, the melting unit power is controlled in such a way as to raise the bath temperature to the desired teeming value. The effect of this furnace holding time on the fading of free graphite nuclei was investigated in experiments where samples of gray cast iron melts were taken in all the molds at times of 5, 17, and 25 minutes after inoculation.

2.3.5 Effect of the Carbide Stabilizer on the Microstructure

To obtain chilled samples, it was necessary to add a carbide stabilizer to the sampled melt. Bismuth and tin were the two available carbide stabilizers, among others, such as chromium, tellurium, and titanium. Table (2-4) gives some data on the employed carbide stabilizers used. Each carbide stabilizer was added to the sampling spoon for melts of gray, nodular and corrosion-resisting austenitic cast irons. As soon as the addition was made, the melt was stirred for three seconds, and then teemed in the sampling molds. In the case of bismuth, no individual steel wire was required for the stirring since bismuth was supplied in the form of coated steel wires. This point made handling of bismuth easier than tin during the melt addition.

2.4 SAMPLING MOLDS

Seven different sampling molds were evaluated for the precision of the spectrochemical analysis of carbon, manganese, phosphorus, sulphur,

TABLE (2-4) Carbide stabilizer additions.

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Addition	Form	Amount Added per Sampling Speon	Concentration in Sample (wt%)	•
Bi -	steel wire coated with approx. 330 mg Bi	1 wire	0.08	
Sn	pellets weighing approx. 110 mg	4 pellets	0.05	

silicon, copper, and magnesium in the cast-iron melts. Table (2-5) describes these molds. The first two molds listed in the table are disposable, while the remainder are permanent. Using disposable molds permits one to avoid contamination from previous heats. Figures (2-1) through (2-6) show the sampling molds.

2.5 SAMPLE AND SPECIMEN PREPARATION

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2.5.1 Sample Preparation for Vacuum Emission Spectrochemical Analysis

Since one of the prime aims of the research work was to relate the precision of the spectrochemical analysis to the sample microstructure, it was considered important to perform both the chemical and the structural analyses on the same sample. Figure (2-7) shows a schematic representation of a typical sample, to be spectrochemically analyzed as well as sectioned for metallographic examination.

Before analyzing the sample on the vacuum emission spectrometer, it was surfaced to obtain a surface which was flat and as free of surface discontinuities (e.g. cracks and cold laps), pores, and shrinkage cavities, as possible. Surfacing was done on a dry belt grinder (aluminum oxide, grit 50). Wet grinding was avoided because it results in water being entrapped in the surface pores of the sample. It is almost impossible for this water to be entirely removed. During sample excitation, any water in the analytical gap may dissociate, giving oxygen, which absorbs the analytical wavelengths of carbon, sulphur, and phosphorous.⁽⁴⁴⁾ Thus, the accuracy of the spectrochemical analysis of these elements is worsened by applying wet-surface grinding. TABLE (2-5) Description of sampling molds and their samples.

ŧ	· · ·	Sample Di	imensions
Mold Type	Mold Description	Thickness, or Height (mm)	Diameter (mm)
1) ceramic ring	alumina ring placed on copper chill plate	30.0	_ 31.0
2) sand shell	shell-molded sand placed on copper chill plate	6.0	(45.0) O.D. (12.0) I.D.
3) air-cooled copper pocket	a pocket in a copper mold machined from a copper block	12.0	34.0
4) copper book	two-piece copper mold clamped together	2.5	28.0
5) cast iron book	two-piece, cast iron mold clamped together	9.0	28.0
6) conical mold	three-piece mold, easily disassembled, made of steel and copper	6.0	58:0
7) water-cooled copper mold	hinged copper book with internal water-cooling	6.0	30.0

FIGURE (2-1) Ceramic ring and sand molds.

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FIGURE (2-2) Air-cooled copper pocket mold.





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FIGURE (2-3) Copper book mold.

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a: assembled mold b: disassembled mold 45



(a)

(b)

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FIGURE (2-4) Cast iron book mold.

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a: assembled mold b: disassembled mold



FIGURE (2-5) Conical mold.

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a: assembled mold b: disassembled mold 47.

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C FIGURE (2-6) Water-cooled copper mold. %a: assembled mold
b: disassembled mold 1.1

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(a) .



(b)

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FIGURE (2-7) Representation of an excitation area and the position for sectioning at A-A for metallographic examination.

D = diameter of sample d = diameter of excitation on sample surface

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All the dimensions are in mm.



In addition, it is very important to apply uniform pressure on the sample when surface grinding in order to obtain a very flat surface. This is necessary because an imperfect surface results in an incomplete sealing of the analytical gap, which then will not be flushed well by the argon. Consequently, the results of the spectrochemical analysis may be incorrect.

2.5.2 Specimen Preparation for Metallographic Examination

The metallographic analysis was done by optical microscopy. Careful attention was paid to the specimen preparation, prior to the metallographic examination, through grinding, polishing, and etching.

a) Grinding

During both rough and fine grinding, water was applied as a coolant to avoid overheating of the ground specimen. (50) Overheating may result in structural changes and graphite pull-out. Rough grinding was done on a silicon carbide belt (grit 80), whereas fine grinding was carried out on a series of silicon carbide belts (grits 166, 320, 400, and 600).

b) Polishing

For cast iron, polishing with diamond-impregnated pastes has been found to be the most satisfactory technique.⁽⁵¹⁾ Diamond pastes of grades 6, 1, and 1/4 micron were used.

c) Etching

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This was normally done by holding the specimen in a pair of nickel tongs and immersing it, with intermittent agitation. Corrosion-resisting austenitic cast iron was etched in a ferric chloride solution (7 g $FeCl_3$ per 100 g water) for 3 minutes, whereas the other kinds of cast irons were etched in 3% nital for 3 minutes.

2.5.3 <u>Sample Preparation for Atomic Absorption</u> Spectrochemical Analysis

It was impossible to analyze for bismuth and tin on the vacuum emission spectrometer because their contents were lower than the lowest analytical limits on the spectrometer. Instead, the atomic absorption spectrometer was employed.

Sample preparation for the atomic absorption spectrochemical analysis involved making drillings in the cast iron samples to obtain ribbons. Preparation of the solutions required for the chemical analysis. followed the following procedures:

- a) Dissolving the sample ribbons in a solution containing concentrated hydrochloric acid along with a few drops of concentrated nitric acid.
- b) Warming the above solution until complete dissolution of the sample ribbons is achieved.
- c) Filtering the solution to separate the non-dissolvable material (e.g. silica and alumina).

d) Bringing the solution, after filtration, to 100 cm³ of volume by using distilled water.

2.6 APPARATUS USED IN THE CHEMICAL ANALYSIS

Atomic absorption and vacuum emission spectrometers were used for the chemical analyses of the carbide stabilizers (Bi and Sn), and of the major compositional elements of cast irons <u>(C, Mn, P, S, Si, Cu,</u> and Mg).

a) Atomic absorption spectrometer

The spectrometer used was a model SP190, PYE UNICAM Ltd. of England. The wavelengths of the analytical lines used to analyze for tin and bismuth were 224.61 and 223.06 NM, respectively. These two lines were used because they give the most accurate chemical analysis.

b) Vacuum emission spectrometer

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The instrument employed was a model DV-2, SPECTROVAC 1000, manufactured by BAIRD Corp., Mass., U.S.A. The excitation source was KH-3, which was developed as a result of extensive research work done in search of an optimum current pulse for excitation of ferrous-based materials.⁽⁵²⁾

The sample stand was a water-cooled copper plate, which achieves long term precision in the chemical analysis.⁽⁵²⁾ The counter electrode was made of silver, with tip angle equal to 90° . The analytical gap was 5 mm. The KH-3 source operated with a unidirectional pulse mode.⁽⁵²⁾ The following specifications are related to this source:⁽⁵³⁾

Input power: 120 V ± 1%, 50/60 Hz, 4.0 A max.

Pulse Output	Excitation	Integration.
peak voltage	950 V	950 V
peak current	275 A	100 A
duration	250 μ s	, 130 µs

Repetition rate: 120 PPs, 60 Hz; 100 PPs, 50 Hz.

The analytical spectral lines are listed in Table (2-6). The Roman numeral after the element symbol indicates the degree of ionization +1. For instance, carbon does not undergo any ionization, and thus its spectral lines are atomic. On the other hand, manganese undergoes a single ionization (i.e. one electron leaves the atom during the excitation), and thus it has ionic spectral lines. The analytical spectral lines were carefully selected when the instrument was designed to ensure the following: ⁽⁵⁵⁾

a) Minimum interference.

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b) Shortest radiation wavelength to allow more available spectrum lines over a shorter focal curve distance, thus giving a more compact spectrometer.

2.7 <u>DETERMINATION OF THE ANALYTICAL CYCLE PERIODS</u> ON THE VACUUM EMISSION SPECTROMETER

The lengths of the analytical cycle periods have an important influence on the accuracy of the spectrochemical analysis. Since the excitation period greatly affects the spectrochemical analysis accuracy, (56) a series of experiments were done to find the best excitation time at the recommended flush and integration periods of 2, and 10 seconds, respectively. An excitation period of 5 seconds was found acceptable TABLE (2-6)

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Spectral lines of the analyzed elements on the vacuum emission spectrometer.

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Element	Radiation Wavelength (A) (46)	Spectrochemical Notation of Radiation Line (54)
Ċ	1930.90	. CI
′ Mn	2568.72	Mn II
P	1782.87	Ρ.Ι
S	1807.34	SI 🔨
Si	2881.58	Si I
Cu	3273.96	Cu I
Mg	2802.70	Mg II
Fe	່ 2599 [°] . 40	Fe II

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since it achieves the shortest analytical time and repeatable analysis as well. The determination of the excitation period is explained in detail in the Appendix A.

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Although the particular spectrometer used was equipped with a minicomputer for direct chemical analysis, it was decided to by-pass this computer and to obtain the spectrochemical analysis from the scalar counts through direct reading from the calibration curves. Although this technique required considerably more time than would have been involved by using the computer, it had the advantage of eliminating , curve-fitting errors by the computer. Therefore, this technique along with the satisfactory analytical cycle periods which were determined, contributes high accuracy to the spectrochemical analysis.

The calibration curves used were drawn with data obtained from the following standard samples (of chemical composition given in Table B-1, Appendix B).

- a) Medium phosphorous iron (sample 1), supplied by B.C.I.R.A., Alvechurch, England..
- b) Low phosphorous iron (samples 2 to 10), supplied by the Research Institute of C.K.D., PRAHA, Czechoslovakia.
- c) High phosphorous iron (samples 11 to 15), supplied byB.C.I.R.A., Alvechurch, England.
- d) Nodular iron (samples 16 to 20), supplied by B.C.I.R.A.,
 Alvechurch, England. The calibration curves are shown in Figures (B-1) to (B-7) in Appendix B.

CHAPTER 3

RESULTS AND DISCUSSION

3.1 PART I: MELTING AND SOLIDIFICATION EXPERIMENTS

A number of experiments were carried out to investigate the influence of some technological factors - such as furnace holding time and casting technique - on the solidification process. The data of these experiments are presented and discussed in the first part of this chapter.

3.1.1 Effect of Furnace Holding Time on the Fading of Free Graphite Nuclei

It was found that 5 minutes was the average furnace holding time. This was the time required to add the ferrosilicon alloy (the graphite inoculant) to the melt bath, and to adjust the melt temperature to the desired value before sampling. A number of experiments were done to investigate the effect of the furnace holding time on the fading of free graphite nuclei. This was carried out by taking samples of gray cast iron at various time intervals after the inoculation. The results are given in Table (3-1), where it is seen that the sample microstructure does depend on the furnace holding time.

Patterson and Lalich⁽⁵⁸⁾ have explained the effect of the holding time after inoculation on the fading of free graphite nuclei. Such fading is attributable to the transformation of rare earth metal carbides (which act as heterogeneous nuclei for graphite formation)



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Holding Time After Fe-Si Addition (min)	Molds Yielding Samples Containing Free Graphite	υ
5	ceramic ring, and air-cooled copper	•
17 🎄	ceramic ring	
25 °	none	

TABLE (3-1) Effect of furnace holding time on sample microstructure. 0

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into sulphides and oxides. The ferrosilicon addition used in this research contained 0.22% calcium, which is adequate; however, there are some other popular proprietary inoculants which have higher contents of rare earth metals.⁽⁵⁹⁾

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3.1.2 Correlation between the Mold Type and the Microstructure

The critical feature of the sample microstructure as far as spectrochemical analysis is concerned, is the presence or absence of free graphite, as well as its distribution within the sample. The distribution of free graphite in the produced samples is discussed in Section 3.1.4°. The correlation between the sampling mold and the microstructure of the various kinds of cast irons made is summarized in Table (3-2).

As mentioned in Chapter 1, the melt composition (11, 12, 21, 29, 30)as well as the rate of solidification, (14) greatly influence the microstructure. Each sampling mold, having its own design and dimensions, offers a different solidification rate. Only the ceramic ring and the air-cooled copper pocket molds gave samples of mottled microstructure for the heats of gray and corrosion-resisting austenitic cast irons. This result is due to the fact that these molds offer a slower cooling rate than the others. The slow rate of solidification, together with the presence of the graphitizing elements (e.g. copper, nickel, and rare earth metal carbides) in the cast iron melts, promoted the graphite precipitation. With magnesium acting as a carbide stabilizer, (12) the formation of free graphite in the produced samples of nodular cast iron occurred only with the ceramic ring mold - which offered the slowest



TABLE (3-2) Correlation between the sampling

mold and the microstructure.

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(a) The non-listed molds yielded samples which were completely chilled, i.e. had no free graphite.

solidification rate. These samples had a chilled layer 0.04 mm thick. As for white cast iron, where no graphitizing elements were added to the melt, all the molds yielded completely chilled samples.

Figure (3-1) to (3-4) show the microstructures of the samples produced in the water-cooled copper mold. The sections which were examined were longitudinal (i.e. parallel to the sample thickness or height) and near the chilled surface. The microstructures of the white, nodular, and gray cast irons consist of pearlitic dendrites in a matrix of cementite. As for the corrosion-resisting austenitic cast iron, the carbides are precipitated between the austenitic dendrites.

3.1.3 Influence of the Graphitizing Elements on the Growth of Free Graphite

The results given in Table (3-3) show the effect of the graphitizing elements on the growth of free graphite flakes in both gray and corrosion-resisting austenitic cast irons. The latter had coarser graphite flakes than the former because of its higher content of graphitizing elements (such as carbon, and the rare earth metal carbides of the Fe-Si alloy added). The difference in the size of the graphite flakes of these two cast iron alloys will be a helpful guide in interpreting the different repeatabilities of the spectrochemical analysis of carbon for these alloys.

Figures (3-5) and (3-6) show the free graphite flakes in a longitudinal section near the chilled surface when the gray and corrosion-resisting austenitic cast irons were cast in ceramic ring molds.



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FIGURE (3-3) Gray cast iron cast in the water-cooled copper mold and etched in 3% nital, X500.

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FIGURE (3-4) Corrosion-resisting austenitic cast iron cast in the water-cooled copper mold and etched in ferric chloride, X500.

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TABLE (3-3) The size and distribution of free graphite flakes near the chilled surface. The cast iron melts were cast in ceramic ring molds.

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-	Type of Cast Iron	The Size and Distribution of Free Graphite Flakes
 	gray • '	Longest flakes are 1/16 in. or less in length at X100. The distribution is interdendritic with random orientation.
	corrosion-resisting austenitic	Longest flakes are 1/16 to 1/8 in. in length at X100. The distribution is interdendritic with random orientation.

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FIGURE (3-5) Gray cast iron cast in a ceramic ring mold and as-polished, X700. The details of the size and distribution of the free graphite flakes are given in Table (3-3).

FIGURE (3-6) Corrosion-resisting austenitic 'cast iron cast in a ceramic ring mold and as-polished, X700. The details of the size and distribution of the free graphite flakes are given in Table (3-3).



3.1.4 Distribution of Free Graphite in the Samples

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It was found that the free graphite is not uniformly distributed in the production samples having mottled structures. Tables (3-4) and (3-5) list the distribution of free graphite in some samples taken in ceramic ring molds. It is obvious that the free graphite becomes coarser and more uniformly distributed in the sample from the chilled surface (Table (3-4)), towards the sample centre (Table (3-5)).

The non-uniform distribution of free graphite on the chilled surface is related to the different nucleation rates, which depend on the cooling rates. The generation of such different cooling rates is due to the inability of the melt streams to cover completely the mold base at once. Consequently, the first stream running over a part of the mold base (or surface) solidifies rapidly with a chilled microstructure. This stream raises the temperature of the mold base in such a way as to retard the solidification of the lagging streams. These lagging streams solidify gray, resulting in the formation of a mottled structure. Such behavior of the melt flow over the mold base (or surface) suggests a mechanism for the formation of cold shuts. ⁽⁶⁰⁾ Figures (3-7) and (3-8) illustrate the formation of cold shuts on the chilled surfaces of two samples.

A chilled surface of any sample can present different paths for heat transfer from the solidifying sample to the air gap between the chilled surface and the mold base, or surface. This explains why different solidification rates, and thus non-uniform distributions of free graphite (namely in the form of patches as listed in Table (3-5)), still exist away from the chilled surface. There is a dissimilarity

TABLE (3-4)

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) The distribution of free graphite in longitudinal sections near the chilled surface, (a). The melts were cast in ceramic ring molds.

Type of Cast Iron	A (mm)	B (mm)	The Distribution of Free Graphite
gray	15	4	The distribution is interdendritic with random orientation. Longest flakes are 1/16 in or less in length at X100.
corrosion-resisting austenitic	20	3	The distribution is interdendritic with random orientation. Longest flakes are 1/16 to 1/8 in in length at X100.
nodular	10	2	5 nodules/mm ² , with the average diameter equal to 10 microns.

(a) In nodular cast iron, a chilled layer of 0.04 mm exists.

A = the width of the examined section.

B = the total distance over which free graphite exists in the examined section.

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TABLE (3-5) The distribution of free graphite in longitudinal sections at a distance of 3 mm from the chilled surface. The melts were cast in ceramic ring molds.

Type of Cast Iron	A (mm)	B (mm)	The Distribution of Free Graphite
gray	15	9	The distribution is uniform with random orientation. Longest flakes are 1/16 to 1/8 in in length at X100.
_ corrosion-resisting			
austenitic	20	7	 The distribution is uniform with random officientation. Longest flakes are 1/8 to 1/4 in in length at X100.
nodular	10	4	10 nodules/mm ² , with the average diameter equal to 18 microns.

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 \mathcal{A} = the width of the examined section.

B = the total distance over which free graphite exists in the examined section.

FIGURE (3-7) Cold shuts spread over the chilled surface. The sample is corrosion-resisting austenitic cast iron cast in a ceramic ring mold. X2.0

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FIGURE (3-8) Cold shuts spread over the chilled surface of the unsurfaced portion of the sample. The analytical burns are seen on the surface of the other portion. The sample is gray cast iron cast in the conical mold. X1.1



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between the size and the distribution of free graphite on the chilled surface and in other sections. As we proceed from the chilled surface toward the sample centre, the free graphite becomes coarser and more uniformly distributed, as shown in Tables (3-4) and (3-5). This occurs because the cooling rate is slower in the sample centre than on the chilled surface.

3.2 PART II: EVALUATION OF THE SAMPLING MOLDS FOR THE REPEATABILITIES OF VACUUM EMISSION SPECTROCHEMICAL ANALYSIS

3.2.1 Statistical Analyses of the Data

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The precision of the vacuum emission spectrochemical analysis is interpreted as the repeatability of the measurement. $^{(61)}$ The precision of a measurement denotes the closeness with which the measurement approaches the average of a series of measurements made under similar conditions. $^{(61)}$ On the other hand, the accuracy of a measurement signifies the closeness with which the measurement approaches the true value. $^{(61)}$ The accuracy is strongly dependent on the bias of the machine used. Though, if a large bias is present, a substantial increase in precision may result in an increase in accuracy. $^{(61)}$

The data from any chemical analysis is expressed as " $\overline{X} \pm t.S/\sqrt{n}$ " where

- t = the t-value at the given degree of freedom and significance level
- S,\overline{X} = the variance and the mean, respectively, of the chemical analysis

n = "the sample size

The precision of the spectrochemical analysis may be given by one of the following two expressions:

$$(i) \quad \frac{t \cdot S/\sqrt{n}}{\overline{X}}$$

(ii)
$$\frac{s}{\overline{x}}$$

In the calculations of the precision, the second expression was chosen because the first one includes the t-value, which depends on the confidence level. Practically, the confidence level ranges from 90 to 95%, and every consumer sets his own level. The precision term will be expressed in the results as % R.V., i.e. percent relative variance which is equal to $(\frac{S}{\sqrt{2}})100$.

It is understood from the above that at a given average of spectrochemical composition the precision of the analysis becomes worse as the variance increases. Hence, it is worthwhile to analyze both the variance and the mean of the spectrochemical analysis statistically. In such statistical analyses, the highest confidence level of 99% was selected, and the sample size was kept equal to 5. The determination of the sample size will be discussed in the next section. The analyses of the variances and the means of the spectrochemical analysis are briefly discussed below.⁽⁶²⁾

a) Statistical analysis of the variances

The tabulated and calculated F-ratios judge whether or not there is a significant difference between two variances. The test of significance which is used for this judgment is the F test. Let

S₁,S₂ = the variances of the spectrochemical analysis for • a given element in the first and second samples • respectively

- v = the confidence level, 99%
- N = the degree of freedom - the sample size - 1

 F_{cal} , $(F_{tab})_{v,N}$ = the calculated and the tabulated F-ratios, respectively

 $F_{cal} = \frac{S_1^2}{S_2^2}, S_1 > S_2^2$ (3-1)

 $(F_{tab})_{v,N} = 15.98$ (63)

IF $F_{cal} > (F_{tab})_{\nu,N}$, the two variances S_1 and S_2 are significantly different.

b), Statistical analysis of the means

Before analysing two means statistically, it is necessary to know whether or not their variances are significantly different. Let

 $\overline{X}_1, \overline{X}_2$ — the means of the spectrochemical analysis for a given element in the first and second samples, respectively

 $n_{1}, n_{2} = the size of the first and second samples, respectively$ $<math>n_{1} = n_{2}$

i) Sample variances not significantly different

If the F test shows that the variances of two samples are not significantly-different, the following procedure can be used to determine whether or not there is a significant difference between the means of the two samples \overline{X}_1 and \overline{X}_2 . First, the variance of the two samples in common should be determined:

$$s^{2} - \frac{(n_{1}-1)s_{1}^{2} + (n_{2}-1)s_{2}^{2}}{n_{1} + n_{2} - 2}$$

 $s_1^2 + s_2^{\cdot 2}$

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Then, a value for the t statistic can be determined as follows:

$$t_{cal} = \frac{\overline{x}_{1} - \overline{x}_{2}}{S(1/n_{1} + 1/n_{2})^{1/2}}$$
$$- \frac{\overline{x}_{1} - \overline{x}_{2}}{S(2/5)^{1/2}}$$

The tabulated t value is equal to

$$(t_{tab})_{\nu,(n_1 + n_2 - 2)} = (t_{tab})_{\nu,8}$$

$$(t_{tab})_{\nu,8} = 3.355$$
 (64)

If $t_{cal} > (t_{tab})_{\nu,8}$, there is a significant difference between the two means.

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ii) / Sample variances significantly different

If the F test shows that the variances of the two samples are significantly different, it is not correct to determine a common variance. The value of t is determined from Equation (3-4), and a value for c is calculated from Equation (3-5) to then be applied in determining the number of degrees of freedom (d.f) which is to be used with the t tables.

$$t_{cal} = \frac{\overline{x_1} - \overline{x_2}}{(s_1^2/n_1 + s_2^2/n_2)^{1/2}}$$
(3-4)
$$c = \frac{s_1^2/n_1}{s_1^2/n_1 + s_2^2/n_2} - \frac{s_1^2}{s_1^2 + s_2^2}$$
(3-5)

where

$$n_1 = r$$

d.f. =
$$\left[\frac{c^2}{n_1 - 1} + \frac{(1 - c)^2}{n_2 - 1}\right]^{-1}$$

(3-6)

IF $t_{cal} > (t_{tab})_{\nu,d.f.}$, there is a significant difference between the two means.

3.2.2 Determination of the Number of Runs

In determining the number of runs, or excitations, for each sample analyzed by vacuum emission spectrometry, it was taken into account that the analyzed layer should have the same uniformity as that found

in industrial practice. Thus we can be sure that the bias - and consequently the precision of the spectrochemical analysis of the analyzed \therefore layer of the produced sample - represent real industrial condition.

As was mentioned in Section 1.3, a lack of precision in the spectrochemical analysis of carbon takes place when the microstructure of the analyzed sample changes from white to gray. In other words, as the percentage of carbon in the form of free graphite increases, the reproducibility of its analysis on a vacuum emission spectrometer decreases. In Section 3.1.4 we noticed that the free graphite becomes coarser and more uniformly distributed as one proceeds from the chilled surface towards the sample centre. Consequently, it is strongly recommended that the layer thickness - or the number of revealed surfaces of the sample to be analyzed - be restricted to that used in foundry practice,

Accordingly, the samples of mottled microstructure might be used to determine the number of excitations. Samples taken in the ceramic ring mold, as listed in Tables (3-1) and (3-2), had free graphite with no chilled surfaces. The sample surface which is used for the spectrochemical analysis receives as many as three excitations. Practically, the production sample is excited three times to obtain the average of the spectrochemical analysis. If the foundryman excites a production sample, taken in a ceramic ring mold, he usually reveals at the most two surfaces when the overlapping of two burns occurs. Therefore, it was reasonable to be restricted to two surfaces of the ceramic ring mold sample, or a number of runs equal to 5, during the chemical analysis.

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3.2.3 <u>Effect of the Microstructure on the</u> <u>Repeatabilities of the Spectrochemical Analysis</u>

The spectrochemical analysis results for the four kinds of cast irons, where no carbide stabilizer was added to the sampled melt, are summarized in Tables (C-1) to (C-12), found in Appendix C. The average spectrochemical analysis for copper of the corrosion-resisting austenitic cast iron melt (7.5%) was higher than the upper analytical limit of the calibration curves (0.7%). Therefore, neither its variance nor repeatability could be determined. Also, the tables of the spectrochemical results do not list any data for the copper book mold. Unfortunately, the copper book mold could not be filled consistently with a melt sample because it had a too narrow ingate.

For a given type of cast iron, there were no significant differences in the means and variances of the spectrochemical analysis from one mold type to another for all the elements except carbon. Such insignificant differences as do occur from one excitation (or run) to another can be related to one or both of the following main sources:

- Instrument stability, which is affected by the purity of the flushed argon.
- 2) Flatness of the surfaced sample. The way in which the above two sources influence the vacuum emission spectrochemical analysis was pointed out in Sections 1.5.1 and 2.5.1.

As for the spectrochemical analysis of carbon, samples which contained free graphite, as given in Table (3-2), yielded significantly larger variances (or poorer repeatabilities, i.e. larger values of %R.V.)

than did samples which froze with no free graphite. An interpretation of this observation can be approached by way of Tables (2-6), (3-4) and (3-5). In Table (2-6) it is understood that

the excitation of carbon when in the form of graphite is easier than when it is in the form of carbides because the carbides - especially Fe₃C - need to ionize before the excitation, while graphite need not do so; and
 carbon, whether elemental or as carbides, is excitable on the vacuum emission spectrometer.

It is concluded from Tables (3-4) and (3-5) that the free graphite is non-uniformly distributed in any analyzed section of the produced samples having free graphite.

Thus, the poor repeatability of the spectrochemical analysis for carbon in samples having free graphite may be attributable to the pull-out of the graphite before its excitation on the vacuum emission spectrometer. The tearing-out of free graphite can take place when the overheating generated in the analyzed sample causes an expansion of the cast iron matrix, which in turn induces thermal stresses which fracture the free graphite. Overheating of the analyzed sample can take place during one, or both, of the following two stages:

> a) The surfacing of the sample using dry grinding. Wet grinding should be avoided, as reviewed in Section 2.5.1, for optimum precision of spectrochemical analysis.

b) The sample excitation,

It is important to note that the reproducibility of the spectrochemical analysis of carbon in the samples having free graphite

strongly depends upon the size of free graphite. Corrosion-resisting. austenitic cast iron samples having free graphite showed poorer reproducibility in the spectrochemical analysis of carbon than did samples of gray cast iron. This can be attributed to the fact (as mentioned, in Section 3.1.3) that the free graphite of the former is coarser than that of the latter. On the other hand, nodular cast iron samples having free graphite have a higher repeatability in the spectrochemical analysis of carbon than those of gray cast iron. This can be due to the fact that the nodular cast iron sample has less free graphite because its melt has lower contents of carbon (which is a graphitizing element) and a higher content of magnesium (which is a carbide stabilizing element) than the melt of corrosion-resisting austenitic cast iron.

3.2.4 The Convenience of Use of the Sampling Molds

It is worth noting, as mentioned in Section 3.2.3, that samples having free graphite, which were analyzed by vacuum emission spectrometry, yielded a poor precision only in the analysis for carbon. Before deciding how to improve the repeatability of the spectrochemical analysis of carbon ' of these samples, it is necessary to review the convenience of use of the various sampling molds.

The molds to be used in the sampling of melts in the foundry must satisfy the following requirements:

> a) The use of water as a coolant should be avoided as any leakage of water during the sampling of the melt could result in an explosion.

- b) The appropriate thickness of the sample should be > 1/2 in or 12 mm. Thin samples overheat during surfacing on the belt grinder, and thus require an interruption to allow for cooling. This, in turn, delays the spectrochemical analysis.
- c) Contamination from the samples of previous heats should be avoided. Disposable molds satisfy this condition.
- d) The melt should have maximum fluidity to fill completely the mold cavity. Molds having narrow ingates usually result in the incomplete filling of the mold cavity.
- e) The chilled surface should have an adequate area to allow for at least three burns (or excitations). In this way, sample surfacing does not have to be done more than once, and thus rapid spectrochemical analysis is feasible.

f) The spectrochemical analysis must have maximum precision. The ceramic ring mold satisfies all the above requirements,
except the last one when its sample has free graphite. On the other
hand, the conical mold fulfils all the above requirements except for
conditions (b) and (c); however, it does satisfy the most important
condition (f):

3.2.5 Improving the Repeatabilities of the Spectrochemical Analysis

After reviewing the convenience of use of the sampling molds in Section 3.2.4, it is apparent that it is important to improve the precision of the spectrochemical analysis of carbon for the ceramic ring samples having free graphite. The carbide stabilizers, tin and

bismuth, as described in Table (2-4), were added to the melt in the sampling spoon. There were two sampling spoons - one for each carbide stabilizer - and the melts used were of gray, nodular, and corrosionresisting austenitic cast irons. The conical, air cooled copper, and ceramic ring molds were evaluated for the repeatability of the spectrochemical analysis of carbon after the addition of carbide stabilizer.

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After treating of the melts with carbide stabilizers, all the samples were completely chilled. Figures (3-9) to (3-11) illustrate the microstructures of gray, nodular, and corrosion-resisting austenitic cast iron melts treated with bismuth and cast in ceramic ring molds. The examined sections represent the surfaces which were excited by the vacuum emission spectrometer.

The results of the spectrochemical analysis are listed in Tables (C-13) through (C-18), in Appendix C. In the case of nodular cast iron, the air cooled copper mold was not evaluated because it had yielded completely chilled samples in previous runs where no carbide stabilizer was added. For a given type of cast iron, the means and the variances of the spectrochemical analysis of all the analyzed elements (including carbon) are not significantly different from one mold type to another.

It should be pointed out that for a given kind of cast iron melt, the reproducibility of the spectrochemical analysis for carbon after treating the melts with the carbide stabilizers - does not vary greatly from one kind of mold to another. Nor is there a great difference between the results obtained from the addition of bismuth and the results obtained with tin. This can be seen in Tables (C-15), (C-18) and (C-19), in Appendix C. Hence, the ceramic ring mold after treating

FIGURE (3-9) Corrosion-resisting austenitic cast iron treated with bismuth and cast in a ceramic ring mold, X500. The etchant was ferric chloride.

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FIGURE (3-10) Gray cast iron treated with bismuth and cast in a ceramic ring mold, X500. The etchant was 3% nital.

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FIGURE (3-11) Nodular cast iron treated with bismuth and cast in a ceramic ring mold, X500. The etchant was 3% nital.

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the melt with a carbide stabilizer is able to fulfil all the requirements set out in Section 3.2.4.

Of the two carbide stabilizers, tin and bismuth, bismuth is sometimes routinely analyzed as it is felt to be deleterious for the formation of the nodules in nodular cast iron. $^{(65)}$ In such a case, it is obvious that tin should be used in the sampling. On the basis of ease of use of the carbide stabilizer, the bismuth coated wires were much simpler to use than the small tin pellets. Thus, no matter which element is used, the wire form is more convenient.

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CHAPTER 4

CONCLUSIONS AND SUGGESTIONS FOR FURTHER WORK

4.º1 CONCLUSIONS

Evaluation of several different molds (which are/in common use by the North American foundry industry) for the precision of the vacuum emission spectrochemical analysis has led to the following conclusions:

> The repeatability of the spectrochemical analysis, for 1) carbon only, depends on the microstructure of the analyzed sample. The analyzed samples having free graphite had significantly higher variances - and, consequently, a worse reproducibility - in the spectrochemical analysis for carbon than those having chilled microstructures. This result can be explained by the fact that the free graphite is non-uniformly distributed in the whole sample (i.e., wit is present in the form of patches), as well as the fact that the free graphite may be pulled out during the dry surfacing, and/or the early stage of the excitation period. However, the reproducibilities of the spectrochemical analysis for the other analyzed elements (such as Mn, P, S, Si, Cu, and Mg) do not depend on the microstructures of the analyzed samples.

2) The ceramic ring and air cooled copper molds gave samples containing free graphite for the melts of gray, and cor-

rosion-resisting austenitic cast irons. The ceramic ring mold was the only one to give a sample having free graphite for the melts of nodular cast iron. All the molds yielded completely chilled samples for the white cast iron melt.

- 3) The levels of graphitizing elements affected the growth of the free graphite. The corrosion-resisting austenitic cast iron had a coarser free graphite (longest flakes 1/16 to 1/8 inch in length at X100) than the gray cast iron (longest flakes 1/16 inch or less in length at X100) when the melts were cast in the ceramic ring molds. This is due to the higher content of the graphitizing elements in the corrosion-resisting austenitic cast iron. Accordingly, when the analyzed samples contained free graphite, the precision of the spectrochemical analysis for carbon in corrosion-resisting austenitic cast iron was worse than that of the gray cast iron.
- 4) The ceramic ring mold is the most convenient one to use, since it satisfies almost all the conditions which allow for a fast and precise spectrochemical analysis. However, the precision of the results of the spectrochemical analysis of carbon was poor when the samples, taken in this mold, contained free graphite. The addition of a small amount of a carbide stabilizer (0.05% Sn or 0.08% Bi) to the melt in the sampling spoon resulted in complete chilling of the samples. Consequently, the precision of the spectrochemical analysis for carbon could be improved by a factor of 5-12.

5) In the addition of the carbide stabilizer to the sampling spoons, there is no preference for the use of bismuth over tin, since both of them improved the precision of the spectrochemical analysis of carbon by about the same order.

4.2 SUGGESTIONS FOR FURTHER WORK

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For a deeper understanding of the process operating and the limitations involved, and to further improve the precision obtained in vacuum emission spectrochemical analysis, the following are suggested as possible areas of investigation:

- Surfacing the sample surface which is adjacent to the adjustable sample clamp to ensure a very good electric contact.
- Correlating the length of the excitation period and consequently the depth of the excited volume - to the average size of the free graphite present within the chilled surface.
- 3) Relating the precision of the spectrochemical analysis of the samples produced to the length of the excitation period. Periods of 5, 10, 15, 20, 25, and 30 seconds may be considered.
- 4) Applying the above suggestions to heats of higher carbon equivalents (C.E. \geq 4.2) than those produced in this research (C.E. \leq 4.0). In this way, it will be possible to make evaluations for eutectic and hypereutectic cast irons.

- 5) Relating the repeatability of the results of the spectrochemical analysis for carbon to the eutectic cell numbers, which are dependent on:
 - a) The cooling rate (or the melt superheat).

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- b) The melt composition, that is, the levels of the graphitizing elements (e.g. C, and the rare earth metals), as well as the content of the carbide stabilizing elements (such as Bi and Sn).
- 6) Studying the ground surface and the burned surface of the analyzed sample by the vacuum emission spectrometer to try to determine if the free graphite is pulled out during the sample surfacing, and/or the sample excitation.

The ceramic ring mold is recommended for use in the experiments suggested above, as it was found to be the most convenient mold.

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APPENDICES

APPENDIX A

Determination of the Analytical Cycle Periods

At the recommended 2-sec. flush and 10-sec. integration periods, the excitation period was varied from 5 to 15 seconds, in intervals of 5 seconds, to determine the best precision of spectrochemical analysis. To avoid^o sample hetrogeneity, which is a source of poor precision, a standard medium phosphorous cast iron sample (of white microstructure) was employed. The chemical composition of this sample (sample No.1) is given in the Appendix B. Tables (A-1) through (A-3) present the repeatabilities of the spectrochemical analysis at the three different excitation periods, where

x̄ = average spectrochemical composition in scalar counts
 S = standard deviation of spectrochemical analysis in scalar counts

%R.V. — precision of spectrochemical analysis expressed as percentage relative variance,

$$R.V. = (\frac{\overline{X}}{S})100$$

Analysis of Data

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The variances of the chemical compositions were analyzed at the 1% significance level and 9 degrees of freedom (since the sample size was equal to 10). Let

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TABLE (A-1)Precision of spectrochemical analysis (expressed as %R.V.)for a 5-sec excitation period.

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Element	C	Mn	Р	s,	(Si) _I	(Si) _{II}
- X	5830	7295	4070	4651	2501	3905
Ś	13.4	43.7	14.7	70	18.3	30.9
%R.V.	0.23	0.60	0.36	1.51	0.73	0.79

TABLE (A-2) Precision of spectrochemical analysis (expressed as %R.V.) for a 10-sec excitation period.

Element	С	Mn	Р	. S	(Si) _I	(Si) _{II}
x	5825	7285 ⁻	4055	4606	1960	3814
S ·	12.8	41.4	15.1	101.9	25.6	40.3

TABLE (A-3) Precision of spectrochemical analysis (expressed as %R.V.) for a 15-sec excitation period.

Élement	C C	Mn	Р	S	(Si) _I	(Si) _{II}
X	5805	7255	3990	4843	2070	3807
S	15.2	46.4	20.4	90.6	24.4	46.3
%R.V.	0.26	0.64	0.51	1.87	1.18	1.22

S₁,S₂ = the variances of the spectrochemical composition of an analysed element at two excitation periods
 ν = the confidence level, 99%
 N = the degree of freedom .
 = the sample size - 1

 F_{cal}, F_{tab} = the calculated and the tabulated F-ratios,

$$F_{cal} = \frac{S_1^2}{S_2^2} , S_1 >$$

$$(F_{tab})_{N,v} = 3.18^{(55)}$$

If $F_{cal} > (F_{tab})_{N,v}$ the variances S_1 and S_2 are significantly different.⁽⁵⁷⁾

Results

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The variances of the chemical compositions of the analyzed elements are not significantly different. Therefore, the excitation period of 5 seconds, being the shortest one, was the most reasonable time. In general, that excitation period gave a more consistent spectrochemical analysis, as expressed by %R.V., than the other two periods.

Generally, the first line of silicon, $(Si)_{I}$ of wavelength ^o ^o 2881.58 Å, had a lower %R.V. (i.e., more repeatable spectrochemical analysis) than the second line, $(Si)_{II}$ of wavelength 3905.00 Å. Therefore, the $(Si)_{I}$ line was used in the computation of the compositions.



APPENDIX B

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Calibration Curves

TABLE (B-1) Chemical compositions of the standard samples used in setting up the calibration curves.

		Chemical Composition (wt%)						
Sample No. C	C	Mn	P ,	S	Si	Cu	Mg	
1	3.60	0.640	0.200	0.130	1.60	0.22	-	
2	2.30	0.510	0.035	0.020	5.45	0.16	-	
3 /	2.00	0.410	0.0/1	0.050	2.40	0.09		
5	2.80	1 770	0 290	0.010	1.90	~ 0.33	-	
. 6	3.10	1.440	0.180	0.091	1.20	0.27		
7	3.30	0.790	0.560	0.130	0.69	0.06	-	
8	3.40	0.380	-	0.007	0.54	1.15	0.100	
9	3.80	0.940	0.050	_	0.51	0.52	0.070	
10	4.40	0.100	0.004	-	0.17	0.70	0.050	
11	2.55	0.420	0.790	0.076	3.12	-	-	
12	3.01	0.760	0.270	0.103	2.37	-	-	
13	3.45	0.990	0. i10	0.029	1.95	-	-	
14	2.74	0.580 °	0.420	0.123	2.70	-	-	
15	3.28	0.220	1.080	0.047	1.58	-	-	
16	3.70	0.580	-	0.005	1.90	0.02	0.070	
17	3.30	0.017	-	-	1.80		0.079	
18	2.88	0.110	-	-	2.94	-	0.061	
19	3.14	0.490	-	-	2.41	-	c 0.028	
20	3.53	0.290	-	-	2.03	-	0.047	

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Ô The calibration curve for carbon. FIGURE (B-1)

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The calibration curve for manganes FIGURE (B-2)

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FIGURE (B-3)

The calibration curve for phosphorus.

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FIGURE (B-4) The calibration curve for sulphur.

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The calibration curve for silicon. FIGURE (B-5)



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The calibration curve for copper. FIGURE (B-6)


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The calibration curve for magnesium. FIGURE (B-7)

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APPENDIX C

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Results of Spectrochemical Analysis

TABLE (C-1) The average compositions of the samples of corrosion-resisting austenitic cast iron. No carbide stabilizer was added to the sampled melt.

`\	· · · ·	Composition (wt %)							
	Mold Type	C,	Mn	τP	Ś	Si	Cu		
	ceramic ring	3.10	0.390	0.0390	0.0620	3.730	> 0.7		
	air-cooled copper	3.03	0.374	0.0304	0.0600	3.761	> 0.7		
) •	sand	3.59	0.410	0.0311	0.0579	3.756	> 0.7		
	cast iron book	3,, 59	0.434	0.0313	0.0600	3.777	> 0.7		
	conical	3.62	0.414	0.0321	0.0600	3.694	> 0.7		
	water-cooled copper	3.59	0.434	0.0311	0.0611	3.754	> 0.7		

TABLE (C-2) The variances of the spectrochemical, analysis of the samples of corrosionresisting austenitic cast iron. No carbide stabilizer was added to the sampled melt.

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0		Variance (wt %)							
Mold Type	С	Mn	Р	S	Si	Cu			
ceramic ring	0.28	0.030	0.0003	0.0031	0.038	••••			
air-cooled copper	0.27	0.031	0.0003	0.0030	0.032	-			
sand	0.02	0.010	0.0005	0.0030	0.030	-			
cast iron book	0.02	0.010	0.0004	0.0010	0.040	-			
conical	0.01	0.019	0.0005	0.0010	0.060	-			
water-cooled copper	0.03	0.010	0.0006	0.0020	0.029	 "			

5) The precision of the spectrochemical analysis, expressed as %R.V., of the samples of corrosionresisting austenitic cast iron. No carbide stabilizer was added to the sampled melt.

Mold Type	С	Mn	P .,	S	Si	Cu
ceramic ring	9.03	7.692	0.7692	5.0000	1.019	-
air-cooled copper	8.91	8.289	0.9868	5.0000	0.851	-
sand	0.56	2.439	1.6077	5.1813	0.799	. –
cast iron book	0.56	2.303	1.2780	1,6667	1.059	-
conical .	0.28	4.589	1.5576	1.6667	1.624	- '
water-cooled copper	0.84	2.304	1,9293	3.2733	0.733	•~

TABLE (C-3)

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TABLE (C-4) The average compositions of the samples of gray cast iron. No carbide stabilizer was added to the sampled melt.

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,	Composition (wt %)							
Mold Type	С	Mn -	P	S	Si	Cu .		
ceramic ring	3.10	0.833	0.4400	0.0900	1.540	0.1300		
air-cooled copper	3.11	0.810	0.4400	0.0800	1.550	0.1300		
sand	3.54	0.833	0.4500	0.0900	1.538	0.1300		
cast iron book	3.54	0.833	0.4501	0.0900	1.558	0.1300		
conical	3.59	0.812	0.4300	0 . 000.	1.580	0.1300		
water-cooled copper	3.54	0.833	0.4300	0.0900	1.601	0.1300		

TABLE (C-5) The variances of the spectrochemical analysis of the samples of gray cast iron. No carbide stabilizer was added to the sampled melt.

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	Variance (wt %)								
Mold Type	С	Mn	_ P	S	Si	Cu			
ceramic ring	0.23	0.035	0.0100	0.0020	0.032	0.0040			
air-cooled copper	0.23	0.030	0.0100	0.0030	0.030	0.0040			
sand	0.05	0.025	0.0260	0,.0020	0.020	0.0040			
cast iron book	0.04	0.030	0.0100	0.0030	0.034	0.0070			
conical	0.02	0,010	0.0200	0.0030	0.020	0.0090			
water-cooled copper	0.03	0.010	0.0100	0.0030	0.010	0.0040			

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The precision of the spectrochemical analysis, expressed as %R.V., of the samples of gray cast iron. No carbide stabilizer was added to the sampled melt. TABLE (C-6)

С	Mn	P	S	Si	Cu
7.42	4.202	2.2727	2.2222	2.078	3.0769
7.40	3.704	2.2727	3.7500	1.939	3.0769
1.41	3,001	5.778	2.2222	1.300	3.0769
1.13	3.601	2.2217	3.3333	2.182	5.3846
0.56	1.232	4.6512	3.3333	1.266	6.9231
0.85	1.201	2.3256	3.3333	0.625	3.0769
•	C 7.42 7.40 1.41 1.13 0.56 0.85	CMn7.424.2027.403.7041.413.0011.133.6010.561.2320.851.201	CMnP7.424.2022.27277.403.7042.27271.413.0015.7781.133.6012.22170.561.2324.65120.851.2012.3256	CMnPS7.424.2022.27272.22227.403.7042.27273.75001.413.0015.7782.22221.133.6012.22173.33330.561.2324.65123.33330.851.2012.32563.3333	CMnPSSi7.424.2022.27272.22222.0787.403.7042.27273.75001.9391.413.0015.7782.22221.3001.133.6012.22173.33332.1820.561.2324.65123.33331.2660.851.2012.32563.33330.625

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TABLE (C-7) The average compositions of the samples of nodular cast iron. No carbide stabilizer was added to the sampled melt.

r F		/	-				
Mold. Type	C	Mn	p	S ,	Si	Cu 、	Mg
ceramic ring	2.31	0.580	0.0256	0.0151	1.821	0.0600	0.0500
air-cooled copper	2.66	0.601	0.0256	0.0132	1.880	0.0630	0.0500
sand	2.67	0.650	0.0266	0.0138	1.964	0.0601	0.0479
cast iron book	2.66	0.660	0.0270	0.0137	1.940	0.0600	0.0521
conical	2.64	0.663	0.0262	0.0145	1.903	0.0675	0.0500
water-cooled copper	2.66	0.660	0.0256	0.0137	1.890	0.0600	0.0500

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TABLE (C-8)

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The variances of the spectrochemical analysis of the samples of nodular cast iron. No carbide stabilizer was added to the sampled melt.

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				Va	riance (wt %)			
	Mold Type	C	Mn	Р	S -	Si	Cu	Mg	
	ceramic ring	0.13	0.061	0.0003	0.0003	0.063	0.0064	0.0030	
	air-cooled_copper	0.01	0.030	0.0003	0.0007	0.042	0.0020	0.0010	
	sand	0.02	0.043	0.0003	0.0003	0.049	0.0040	0.0010	
	cast iron book	0.02	0.029	0.0004	0.0004	0.060	0.0040	0.0010	
	conical	0.01	0.042	0.0005	0.0006	0.045	0.0036	0.0010	
	water-cooled copper	0.01	0.037	0.0003	0.0004	0.065	0.0040	0.0013	
			1			,			

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9) The precision of the spectrochemical analysis, expressed as %R.V., of the samples of nodular cast iron. No carbide stabilizer was added to the sampled melt.

							· · · · ·	
Mold Type	C	Mn	P	S	Si	Cu	Mg	-
ceramic ring	5`.63	10.517	1.1719	1.9868	3.460	10.6670	6.0000	-
air-cooled.copper	0.38	4.992	1.1719	5.3030	2.234	3 . 1746	2.0000	
sand	0.75	6.615	1.1278	2.1739	2.495	6.6556	2.0877	
cast iron book	0.75	4.394	1.4815	2.9197	3.093	6.6667	1.9194	
conical	0.38	6.335	1.9084	4.1379	2.365	5.3333	2.0000	ı
water-cooled copper	0.38	5.606	1.1719	2.9197	3.439	6.6667	2.6000	
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TABLE (C-10)

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The average compositions of the samples of white cast iron. No carbide stabilizer was added to the sampled melt.

	Composition (wt %)								
Mold Type	C	Mn	P	S	Si	Cu '			
ceramic ring	3.06	0.569	0.0900	0.0900	0.650	0.1500			
air-cooled copper	2.99	0.578	0.0900	0.0900	0.650	0.1500			
sand	3.09	0.585	0.1024	0.0900	0.656	0.1562			
cast iron book	3.11	0.614	0.1004	0.0941	0.632	0.1562			
conical	3.14	0.59Õ	0.0962	0.0983	0.644	0.1500			
water-cooled copper	3.02	0.596	0.0942	0.0978	0.650	0.1600			

TABLE (C-11) The variances of the spectrochemical analysis of the samples of white cast iron. No carbide stabilizer was added to the sampled melt.

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••••••••••••••••••••••••••••••••••••••			Variance (wt %)					
Mold Type	С	Mn	P	S	Si	Cu		
ceramic ring	0.05	0.014	0.0030	0.0020	0.003	0.0030		
air-cooled copper	0.03	0.005	0.0020	0.0020	0.010	0.0030		
sand	0.05	0.017	0.0050	0.0060	0.010	0.0040		
cast iron book	0.05	0.012	0.0020	0.0020	0.010	0.0030		
conical	0.05	0.013	0.0040	0.0040	0.010	0.0030		
water-cooled copper	0.02	0.013	0.0020	0.0053	0.010	0.0100		

TABLE (C-12) The precision of the spectrochemical analysis, expressed as %R.V., of the samples of white cast iron. No carbide stabilizer was added to the sampled melt.

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Mold Type	Ċ	Mn	P	S	Si .	Cu
ceramic ring	1.63	2.460	3,3333	2.2222	0.462	2.0000
air-cooled copper	1.00	0.865	2,2222	2.2222	1.539	2.000
sand	1.62	2.906	4,8828	6.6667	1.524	2.5608
cast iron book	1.61	1.954	1.9920	2.1254	1.582	1.9206
conical	1.59	2.203	4,1580	4.0692	1.553	2.0000
water-cooled copper	0.66	2.181	2.1231	5.4192	1.539	6,2500

- TABLE (C-13)	The average compositions when bismuth
•	(0.08% Bi) was added to the sampled melt.

/		Composition (wt %)							
Type of Cast Iron	Mold Type	С	Mn	P	S	Si	Cu	Mg	
corrosion-	ceramic ring	2.78	0.429	0.0201	0.0230	3.712	> 0.7	-	
resisting austenitic	air-cooled copper conical	2.77 2.83	0.429 0.460	0.0205	0.0243 0.0249	3.728 3.830	> 0.7 [*] > 0.7	-	
	ceramic ring	3.12	0.760	0.3700	0.0760	1.653	0.1200	_	
gray	air-cooled copper conical	3.07 3.13	0.737 0.772	0.3500 0.3890	0.0778 0.0746	1.610 1.682	0.1120 0.1208	-	
nodular	ceramic ring	3.20	0.529	0.0208	0.0089	1.875	0.0370	0.0286	
	conical ,	3.19	0.576	0.0222	0.0083	1.991	0.0392	0.0298	

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TABLE (C-14)The variances of the spectrochemical
analysis when bismuth (0.08% Bi) was
added to the sampled melts.

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Type of Cast Iron	Mold Type	С	Mn	P	S	Si	Cu	Mg
corrosion- resisting austenitic	ceramic ring air-cooled copper conical	0.02 0.05 0.04	0.017 0.019 0.015	0.0004 0.0004 0.0007	0.0010 0.0020 0.0009	0.090 0.079 0.057	、 <mark>-</mark> 、 - 、 ,	
gray	ceramic ring aìr-cooled copper conical	0.03 0.06 0.03	0.034 0.033 0.017	0.0100 0.0120 0.0160	0.0040 0.0030 0.0030	0.042 0.051 0.030	0.0060 0.0050 0.0070	- - -
nodular	ceramic ring conical	0.03	0.024 0.040	0.0008	0.0003- 0.0004	0.061 0.098	0.0019 0.0027	0.0009 0.0006

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TABLE	

LE (C-15) The precision of the spectrochemical analysis, %R.V., when bismuth (0.08% Bi) was added to the sampled melts.

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Cast Iron	Mold Type	С	Mn	Р	S	Si	Cu	Mg
corrosion-	ceramic ring	0.72	3.963	1.9900	4.3478	2.425	· - ,	-
resisting ° austenitic	air-cooled copper conical	1.81	4.429 3.261	1.9512 3.2864	8.2305 3.6145	2.119	-	-
	·						** · · · · · · · · · · · · · · · · · ·	
	ceramic ring	0.96	4.474	2.7027	5.2632	2.541	5.0000	-
` gray	air-cooled copper	1.95	4.478	3.4286	3.8560	3.168	4.4640	-
9	conical	0.96	2.201	4.1131	4.0214	1.784	5.7947	-
	ceramic ring	0.94	4.537	3.8462	3.3708	3.253	5.1351	3.1469
nodular	conical	0.31	6.944	3.1532	4.8193	4.902	6.8878	2.0134

		Composition (wt %)								
Type of Cast Iron	Mold Type	C	Mn ^	Р	S	Si	Cu	Mg		
corrosion-	ceramic ring	2.45	0.422	0.0202	0.0307	3.524	> 0.7	1		
resisting	air-cooled copper	2.59	0.423	0.0198	0.0382	3.530	> 0.7	-		
austenitic	_ conical	2.53	0.448	0.0206	0.0349	3.604	> 0.7	-		
<u></u>	ceramic ring	2.99	0.765	0.3640	0.0800	1.913	0.1460	-		
grav	air-cooled copper	2.99	0.745	0.3692	0.0804	1.971	0.1432	-		
.	conical	3.05	0.776	0.3800	0.0862	1.936	0.1514	` -		
natular	ceramic ring	3.26	0.562	0.0239	0.0116	1.376	0.0360	< 0.02		
noquiar	conical - 3	3.31	0.614	0.0243	0.0119	1.418	0.0422	< 0.028		

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TABLE (C-16) The average compositions when tin (0.05% Sn) was added to the sampled melts.

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Type of Cast Iron	Mold Type	, C	Mn	P ,	S	Si	Cu	Mg
corrosion- resisting austenitic	ceramic ring air-cooled copper conical	0.02 0.03 0.03	0.024 0.016 0.013	0.0004 0.0003 0.0002	0.0021 0.0024 0.0025	0.033 0.099 0.036	-	- -
gray	ceramic ring air-cooled copper conical	0.03 0.03 0.05	0.031 0.033 0.016	0.0090 0.0190 0.0240	0.0040 0.0040 0.0050	0.040 0.040 0.012	0.0050 0.0030 0.0060	
nodular	ceramic ring conical	0.03	0.051 0.025	0.0003 0.0002	0.0007 0.0005	0.024 0.021	0.0061 0.0050	ح ال _ا ب

 TABLE (C-17) The variances of the spectrochemical analysis when tin (0.05% Sn) was added to the sampled melts.

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FABLE (C-18)	The precision of the spectrochemical
a	analysis when tin (0.05% Sn) was
	added to the sampled melts.

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Type of		•	•	۰				
Cast Iron	Mold Type	C	' Min	Р	S	Si ·	Cu	Mg
corrosion-	ceramic ring	0.82	5,687	1.9802	6.8404	Ò.936	- ,	-
resisting	air-cooled copper	1.16	3.783	1.5152	6.2827	2.805	-	
austenitic	conical	1.19	2,902	0.9709	7.1633	1.007	-	-
*	ceramic ring	1.00	4.052	2.4725	2.0910	2,091	3. 4247	
grav	air-cooled copper	1.00	4,430	5,1463	4.9751	2.029	2.0950	-
6 , 2 , 1 ,	conical	1.64	2.062	6.3158	5.8005	0.620	3.9630	-
•	ceramic ring	0.92	9.075	1,2552	6.0345	1.744	16,9440	
nodular	conical	0.60	4.072	0.8231	4.2017	1.481	11.8480	~

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	Corros Resis Austen Cast Iron	ion- ting itic	Gray Cast Iron		Nodular Cast Iron		White Cast Iron	
Carbide Stabilizer	%R.V.	0.I.P.	%R.V.	0.I.P.	%R.V.	0.I.P.	%R.V.	0.I.P.
none	9.03	· -	7.42	-	5.63	-	1.63	, , , , , , , , , , , , , , , , , , ,
bismuth '	~0.72	11.54	0.96	6.73	0.94	4.99	-	-
tin	0.82	10.01	1.00	6.42	0.92	5,12	- `	-

The concentrations of bismuth and tin in the sampled melts were 0.08, (a) and 0.05 percent, respectively.

0.I.P. = $\frac{(\$R.V.)_1 - (\$R.V.)_2}{(\$R.V.)_2}$

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where $(R.V.)_1$ and $(R.V.)_2$ = the percent relative variances before and after adding the carbide stabilizer, respectively.

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