



ARA  
INFORMATION

Issue 2 ■ Fall 2023

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# Welcome



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**WELCOME TO THE LATEST EDITION OF "ARA INFORMATION"**, where we delve deep into the fascinating realms of the mining and metal industries. In this edition, we have curated a collection of insightful articles that shed light on cutting-edge analytical methods, innovative techniques, and the ever-evolving landscape of these crucial sectors.

The "ever-evolving" is the only constant component in the business environment of today's world, and Mining and Metal Industries must align themselves with these wide-ranging, continuous, and inclusive development requirements of The Fourth Industrial Revolution. Smart technologies, Machine learning, Artificial intelligence, 3D printing, ... promise sustainable and green industries to humanity.

Our journey begins with an exploration in the chapter of Quality Control with the "Determination of Ferrous Oxide in Iron Ore Pellets with Magnetic Method." This article uncovers the intricacies of quantifying Ferrous oxide content in iron ore pellets, demonstrating the magnetic-characteristics allure in analytical science. The foundation of precise analysis lies in effective sample division, and our article on "Sample Division by Modern Analytical Methods" reveals the latest innovations in this essential aspect of analytical chemistry.

In the quest to understand the very essence of metal alloys, the Chapter Know-How serves The Article "Comparison of Different Elemental Analysis Techniques for the Characterization of Metal Alloys" presents a comprehensive survey of the three most-important methods at our disposal, guiding us toward the most effective approaches for metal alloy characterization. We also illuminate -some challenges faced in elemental analysis with "Light Elemental Analysis in Metal Alloys - Elements That Challenge Handheld XRF and Non-Mobile Spark OES." Here, we explore the limitations and advancements of handheld X-ray fluorescence (XRF) and non-mobile spark optical emission spectrometry (OES) techniques. For those fascinated by the allure of precious metals, "Determination of Gold by Stripping Voltammetry" promises to be a golden exploration into this fascinating technique and challenges involved in unlocking the secrets of this coveted element. Since Surface finishing processes hold a significant place in the metal industry, "Comparison of HPLC and IC for the Determination of Anions and Organic Acids in Plating Baths" dives deep into the world of anion and organic acid determination, comparing the merits of two prominent analytical techniques.

Moving forward, we venture into the realm of Environmental Monitoring and Safety with "Detection of Multiple Heavy Metals by Stripping Voltammetry". Here, we uncover the power of stripping voltammetry in precise detection and quantification of heavy metals, a crucial endeavor for safeguarding both industry and environment. Finally, "Determination of Hexavalent Chromium as an Environmental Pollutant in Metal Industries" addresses identification and quantification of one of the world's most serious environmental concerns due to its long persistence in the environment and highly deadly nature of this element for living organisms.

As we embark on this analytical journey through the mining and metal industries, we invite you to delve into the depths of innovation, discovery, and precision that define these fields. We trust that knowledge and insights shared in this edition will inspire and inform, whether you are a seasoned industry professional or an enthusiastic explorer of the world of metals. Welcome to "ARA Information," where the world of mining and metal meets the cutting edge of analysis.





## SPECTROSCOPY APPLICATION CHALLENGE WINNERS

to bring a spectroscopy application challenge to the researchers and scientists each year

The “Spectroscopy Challenge Award” aims to foster regional competition and provide a comprehensive evaluation platform for ongoing research in various specialized fields, using modular spectroscopic systems. This initiative seeks to recognize and promote excellence in spectroscopy research within the scientific community.

The subject of this challenge is showing the power of modular spectroscopy supplied by ARA Spectron / manufactured by Ocean Optics and how it can enable scientists to explore a wealth of information with the relatively simple measurement of how light interacts with a sample. Researchers from GCC can participate for a chance to win 10,000.00 AED by submitting an abstract of their Spectroscopy research with a photo of the used set up.

The Spectroscopy Application Challenge for the year 2023 has officially closed and in this issue of our magazine, we are honored to introduce our winners.

Spectroscopy-based technologies have achieved remarkable successes in all walks of life, and continued to show their value as backbones in scientific research and real-world applications. One of the important challenges is we consume too much in an unsustainable manner, and transitioning to sustainability is hard. Sustainability and in a broader view the sustainability strategy attempts to bridge social science with environmental science and with the technology of the future. It’s time to think about protecting the environment, renewable fuel sources, reducing carbon emissions, deforestation, food and water insecurity, and keeping the fragile ecosystems of our planet instability. So that we can protect our natural environment, and human and ecological health, while driving innovation and not compromising our way of life. Scientific research empowers us to explore and helps us drive a brighter tomorrow.

We, here in ARA Spectron, are seeking to help scientists to make breakthrough discoveries and bring more sustainability by developing new applications that improve the quality of human life. Hence, we decide

**Check out our winners below:**

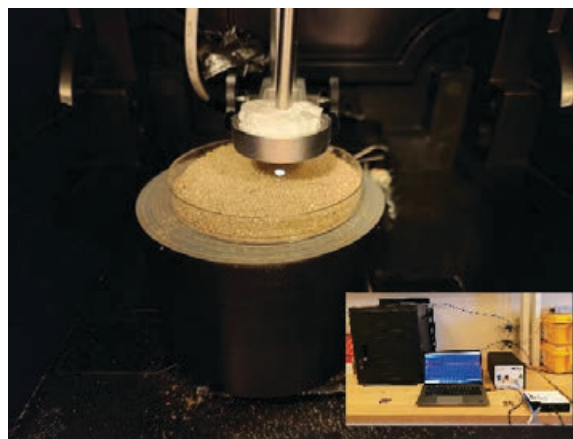
**1<sup>st</sup> Place Spectroscopy Application winner 10,000.00- AED cash**

**KHALIFA UNIVERSITY, Abu Dhabi, UAE**

Submitted by Abdel Rahman Satei Hussein Alsaleh

Summary: Prediction of Soil Organic Carbon in Arid Regions Using Hyperspectral Spectroscopy: UAE Case Study

Soil organic carbon (SOC) plays a pivotal role in numerous ecological processes and holds significant implications for soil health, carbon cycling, and mitigation of climate. Therefore, the accurate measurement of SOC is essential for understanding its spatial distribution, monitoring changes over time, and making informed management decisions. Traditional methods of SOC measurement, such as titration, colorimetric, and loss of ignition methods, are labor-intensive, time-consuming, and often limited in spatial coverage. Therefore, this study adopted the spectral analysis method that has become more popular with undeniable advantages over traditional methods to estimate SOC. The objective of this study is to use these spectral reflectance measurements to develop models that can predict SOC. A total of 59 soil samples were collected from the agricultural fields in the United Arab Emirates (UAE) and analyzed in a laboratory for testing the SOC using the Walkley and Black wet combustion method. Spectroscopic measurements for these soil samples were collected under stable laboratory conditions using two instruments to cover the full range of wavelength. This research is the first step toward developing a spectral library of materials in the UAE.



**2<sup>nd</sup> Place Spectroscopy Application winner- 3,000.00 AED coupon for next purchase**

**King Abdulaziz University, Jeddah, KSA**

Submitted by Reem M Altuwirqi

Summary: Classification of Edible Salts Using Raman Spectroscopy Coupled with Principal Component Analysis

Raman Spectroscopy is an effective optical technique for molecular vibration modes analysis. It has numerous advantages such as being easy and rapid with no loss of accuracy and can be applied to diverse samples. A Raman spectrum can be regarded as a fingerprint to the structure of molecules which assists in characterizing materials. In this work, Raman Spectroscopy coupled with an exploratory tool such as principal components analysis (PCA) is applied for identifying and categorizing 24 edible salts available in the local market of Jeddah, Saudi Arabia. The results show the effectiveness of Raman spectroscopy and PCA analysis in discriminating the kinds of edible salts based on their origin (rock or sea). This suggests the difficulty in distinguishing the chemical treated refined salts. This study could be used to classify edible salts based on their origin.



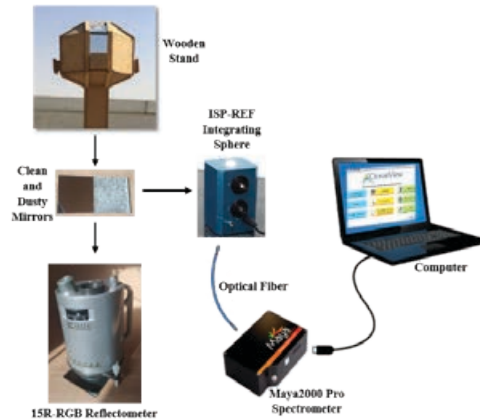
**3<sup>rd</sup> Place Spectroscopy Application winner- 2,000.00 AED coupon for next purchase**

**University of Sharjah, Sharjah, UAE**

Submitted by Ahmed Amine Hachicha

Summary: The use of Ocean Optics miniature Maya2000 Pro Fiber Optic Spectrometer to determine the reflectance of CSP mirrors

This research was conducted at the university of Sharjah in the objective to measure the soiling loss in the reflectivity of CSP mirrors and determine its impact under UAE and similar weather conditions. In order to accurately measure the solar weighted specular reflectivity, both specular reflectivity and hemispherical solar weighted reflectivity should be determined. Several mirrors were placed in a wooden stand at different tilt angles and directions at the university of Sharjah. This work could help the in better understanding the dust effect on CSP performance under desertic climate and therefore assists in selecting the adequate cleaning strategies and frequencies.



We thank everyone who applied to the Spectroscopy Application Challenge this year and let's remember that the only way to preserve our resources is to live in harmony with nature. By compromising nature, we are compromising our growth, development, and even survival.



# DETERMINATION OF FERROUS OXIDE in “Iron Ore Pellets” with the Magnetic Method as an Alternative to the Wet Chemistry Method



**Farid Sheikh-Hasani**  
MSc of polymer chemistry  
Particle & Polymer Testing Product Manager



## **Abstract:**

**DURING THE IRON** Ore Pelletizing process, the ferrous oxide (FeO), which is present in magnetite ( $\text{FeO-Fe}_2\text{O}_3$ ), must be oxidized and converted into ferric Oxide  $\text{Fe}_2\text{O}_3$  hematite. Wet Chemistry is the common method to measure the ferrous oxide in iron ore Pellets. These methods are time-consuming, destructive, and have adverse environmental effects. Also, due to the low amount of FeO in the composition, the chemical methods have a noticeable error.

The magnetic method was studied due to the difference

in the magnetic saturation property of magnetite and hematite, the experimental sample of the FeO magnetic measuring device was made, the preliminary investigations were done and finally, a “FeO Magnetic Analyzer” was made with unique features.

Various reproducibility Analyzes and inter-laboratory comparisons were done. Statistical investigations showed that the FeO Magnetic Analyzer has appropriate accuracy and precision. Also, higher speed and lower cost indicate an acceptable analyzer that is made for the first time in Mubarak Isfahan Steel.

## Introduction:

During the Iron Ore Pelletizing process, the iron ore is oxidized and due to the nature of the direct reduction process, effort is made to have as much of the iron in the Iron Ore Pellets as hematite (trivalent iron oxide) or the same as  $\text{Fe}_2\text{O}_3$ .

In the Direct Reduction of Iron Process, the iron in the Iron Ore Pellets is converted from  $\text{Fe}_2\text{O}_3$  to  $\text{Fe}_3\text{O}_4$ , then to  $\text{FeO}$ , and finally to  $\text{Fe}$  metal. During the Direct Reduction Process, gas penetration and continuous process are very important. For example, although  $\text{Fe}_2\text{O}_3$  is converted into  $\text{Fe}_3\text{O}_4$  and  $\text{Fe}_3\text{O}_4$  is also converted into  $\text{FeO}$ , the  $\text{FeO}$  present in the initial  $\text{Fe}_3\text{O}_4$  does not undergo the Reduction Process due to its crystalline structure and low porosity, and it remains almost without any change at the end of the reduction stages.

The initial magnetism of the structure is slag in the reduction process, which is also lost as slag in steelmaking furnaces. Therefore, the most cost-effective way is to convert  $\text{Fe}_3\text{O}_4$  to  $\text{Fe}_2\text{O}_3$  in the Iron Ore Pelletizing process even though magnetite ( $\text{Fe}_3\text{O}_4$ ) itself includes hematite and  $\text{FeO}$ . As the result . . . ,  $\text{FeO}$  or bivalent iron must be oxidized in the Ore Pelletizing process, and be converted into  $\text{Fe}_2\text{O}_3$ . Accurate and fast measurement of  $\text{FeO}$  amount is an important topic for Iron Ore Pelletizing factories because it measures the degree of cooking of pellets.

The content of  $\text{FeO}$  in the Iron Ore Pellets is less than 5% (weight percent) according to the Industrial Experiments in the Iron Ore Pelletizing factories. In the Wet chemical Analysis Method of  $\text{FeO}$ , the sample is dissolved in Chloride Acid, a mixture of Sulfuric Acid & Phosphoric Acid is added and the mixture is diluted with distilled water. The Ferrous oxide is determined with Potassium Dichromate Titration by Diphenyl Amino Sulfonate.

This research is based on the difference in the magnetic properties of  $\text{Fe}_3\text{O}_4$  and  $\text{Fe}_2\text{O}_3$ . The net magnetic moment in the saturation state for magnetite is equal to 0.98 Bohr magneton and 0.0095 Bohr magneton for hematite. If we place a material consisting of hematite and magnetite in a sufficiently strong magnetic field in the direction of gravity and weigh the sample, the weight shown by the scale is equal to the initial weight plus the force which is produced by magnetic property of Hematite and Magnetite:

$$1) \quad W_t = W_o[1 + AX + B(100 - X)] \frac{1}{100}$$

$$2) \quad X = 103.04 \frac{W_t}{W_o} - 104.02$$

In equation 1,  $a$  is the magnetic moment of magnetite in the state of magnetic saturation and is equal to 0.98 Bohr magneton.  $B$  is the magnetic moment of saturation of hematite and is equal to 0.0095 Bohr magneton, while  $W_t$  is the total weight at the time of being placed in the magnetic field. Also,  $W_o$  is the initial weight of the sample.

$$1) \quad W_t = W_o[1 + 0.98X + 0.0095(100 - X)] \frac{1}{100}$$

Therefore:

$$2) \quad X = 103.04 \frac{W_t}{W_o} - 104.02$$

In this way, the percentage of magnetism is determined. According to the molecular weight of magnetite and iron oxide II, the percentage of iron oxide II is determined.

$$\text{FeO} = 56 + 16 = 72$$

$$\text{Fe}_3\text{O}_4 = 3 \times 56 + 4 \times 16 = 232$$

$$3) \quad \text{FeO} = \text{Fe}_3\text{O}_4 \times 72 / 232$$

Elements and compounds with the ability to be magnetized affect the above equations by not being able to be precisely measured. Among these elements, cobalt, chromium, nickel, zinc, and titanium have the most effect in distorting the final measurement. The effect of these elements can be offset by applying a correction factor that is done by calibrating the device with standard samples. The important point in this process is to create a uniform and stable magnetic field downwards. Figure 1 shows these two electromagnets. An aluminum sheet is used to remove the effect of the magnetic field on the scale.

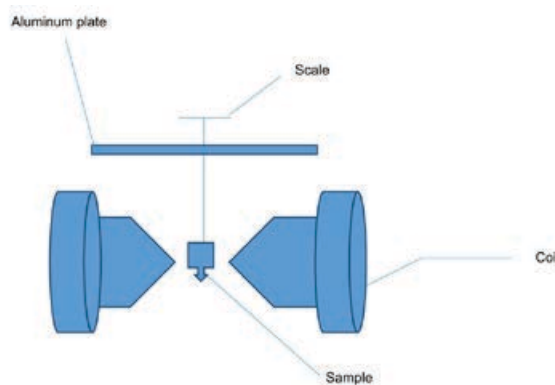


Figure 1. Schematic diagram of two electromagnets in the middle of which there is a fixed magnetic field facing downwards

### Laboratory conditions:

Figure 2 shows the device built and used in this research. This device includes an electric current generator, a twin electromagnet, an Analytical Balance with an accuracy of 0.1 mg (along with a glass tube that gives the scale the ability to weigh at the bottom and top), and a computer that includes the software of the device. Also, a small glass sampling capsule is needed to place the powder sample inside.

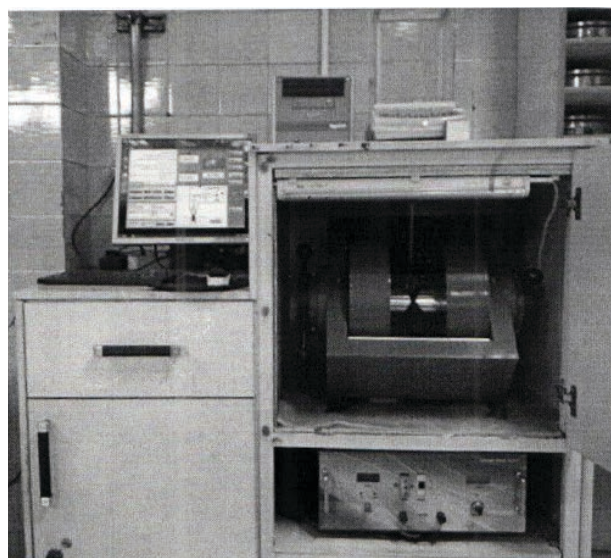


Figure 2. FeO Magnetic Analysis Setup



The electric current generator is designed in a way that during the test “constant electric current” is implemented. The electric magnet is built in such a way that as a result of the constant electric current, in the location of the sample capsule (at the bottom), it creates a constant and uniform magnetic current with an intensity of 0.5 tesla towards the bottom (The field is controlled by a tesla meter.). In order to perform the test, first the weight of the empty capsule is recorded ( $C_0$ ), then the weight of the empty capsule is recorded in the magnetic field ( $C$ ) to complete the calibration related to the empty capsule. In the next stage, the

sample is poured into the capsule and it is weighed ( $M_0$ ) outside the magnetic field by the Analytical Balance (above). After that, the sample capsule is placed in the magnetic field and weighed ( $M$ ). Now, the calculations related to the change in the weight of the sample due to the magnetic field are done.

$$4) \quad W_t - W_o = (M - C) - (M_o - C_o)$$

Now, according to equations 2, 3, 4 and made corrections related to different elements (by comparing with standard samples), the percentage of FeO is determined.

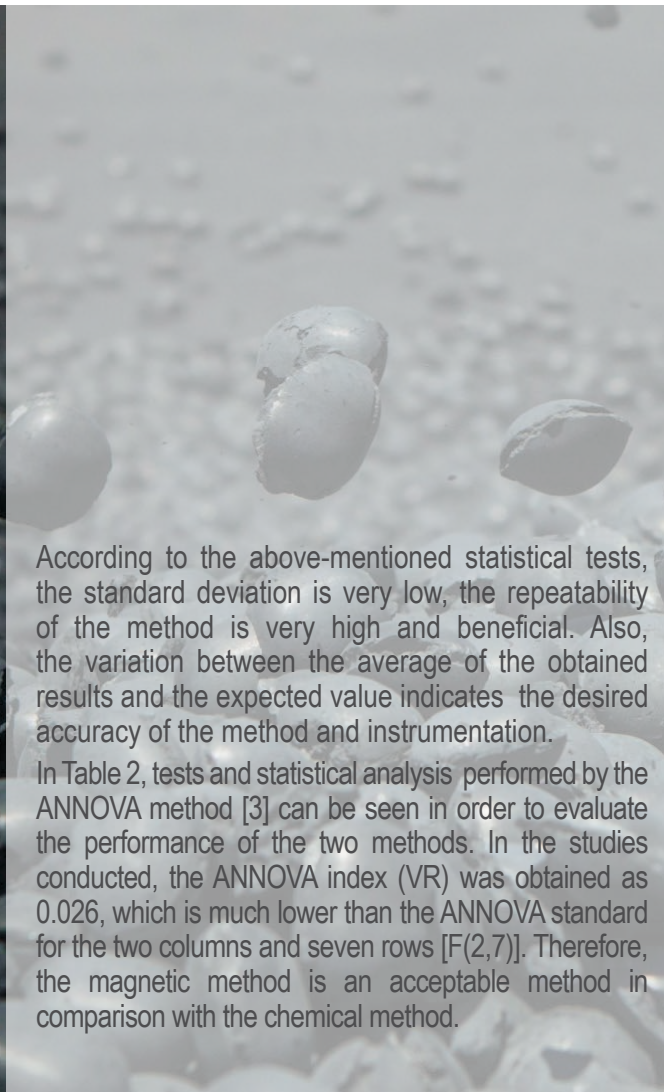
### Results & Discussion (conclusion):

Table 1 shows the results of reproducibility tests to determine the percentage of FeO by magnetic method on three standard samples RM1, RM2 and RM3. According to the repeatability tests, the accuracy of the Analytical Instrument and method is determined. These standard samples are a mixture of pure hematite and 97 percent magnetite, the remaining elements of which are:

1% SiO<sub>2</sub> → 0.5% Al<sub>2</sub>O<sub>3</sub> → 1.5% CaO+MgO  
(Produced by Alfa Aesar, Lot #: 54023336 / CAS #: 1317) They were prepared in a manner that the weight percentage of FeO in these samples is as follows:  
RM1=0.310%, RM2=0.430% and RM3=0.550%

Sample \ Repetition	RM1	RM2	RM3
	1	0.315	0.450
2	0.290	0.444	0.564
3	0.310	0.436	0.520
4	0.305	0.403	0.555
5	0.330	0.420	0.540
6	0.314	0.426	0.550
7	0.320	0.444	0.560
Average	0.312	0.342	0.548
Standard Deviation	0.0019	0.0026	0.0023

Table -1. The Results of Repeatability tests



According to the above-mentioned statistical tests, the standard deviation is very low, the repeatability of the method is very high and beneficial. Also, the variation between the average of the obtained results and the expected value indicates the desired accuracy of the method and instrumentation.

In Table 2, tests and statistical analysis performed by the ANNOVA method [3] can be seen in order to evaluate the performance of the two methods. In the studies conducted, the ANNOVA index (VR) was obtained as 0.026, which is much lower than the ANNOVA standard for the two columns and seven rows [F(2,7)]. Therefore, the magnetic method is an acceptable method in comparison with the chemical method.

method	Chemical	Magnetic	total
sample			
1	0.31	0.35	0.66
2	0.59	0.54	1.13
3	0.35	0.39	0.74
4	0.44	0.40	0.84
5	0.27	0.22	0.49
6	0.79	0.72	0.151
7	0.35	0.36	0.71
n	6	6	12
$\sum x$	3.1	2.98	6.08
$(\sum x)^2$	9.61	8.8804	18.49
$((\sum x)^2)/n$	1.602	1.4801	3.0817
$\sum x^2$	1.1908	1.0621	2.2529
$\sum x^2/n$	0.19847	0.177017	0.3755
$\frac{\sum x^2}{n}$	0.06402	2.2201	2.2841
df1		2	
df2		12	
Ssb		0.001	
ssw		0.829	
VR		0.026	
F(2,7)=4.74		F(2,7) > VR	

Table 2 - Statistical studies performed by ANNOVA method in order to evaluate the performance of two methods



## Conclusion

Determining the percentage of FeO in Iron Ore Pellets by magnetic method gives acceptable results in comparison with the chemical method of the standard sample given in Table 2 with satisfactory accuracy.

The reproducibility of FeO results by the magnetic method is better than by the chemical method, because the standard deviation in the magnetic method according to Table 1 is X.XXX, but in chemical method it is X.XX.

The cost, time consumption, and environmental pollution of FeO analysis by the magnetic method is less than the chemical method because, in the chemical method, which is time-consuming, expensive chemicals are used, and from this point of view, the magnetic method is preferable.

The device for determining the percentage of FeO by magnetic method is a reliable and acceptable device.

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## SAMPLE DIVISION FOR Modern Analytical Methods



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**INSTRUMENTS USED** to measure particle size have now achieved a degree of accuracy which was inconceivable years ago and the tolerances are constantly being reduced. The introduction of software graphics coupled with multitasking operating systems together with ever more powerful computers has led to higher reliability and reproducibility than ever before.

But in practice, the situation is sometimes a little more complex. Although the analysis promises accuracy and precision, results inexplicably occur which raise doubts about the highly praised instruments. However, the true reason for the anomalous results is not in the testing process with a floating decimal point

or operator error; it is simply due to the protocol of the preparation of the samples before they are presented to the measuring system.

It is an amazing fact that the market for high-precision fully automatic analyzers is constantly growing, whilst no one seems to be concerned about the preparation and collecting of the samples, factors which are equally if not more important in obtaining a reliable result. Enlightenment on the aspect of particle size has improved as higher levels of accuracy have been achieved. The emphasis has now shifted to the sample preparation aspect of the measuring process.

### The Task in Hand:

The practical use of expensive, high-quality analyzers is directly related to the sample presented for analysis. The analysis error always includes both sampling and measuring errors. Based on the law of error propagation, the ascertained total error in the value of the results is:

$$S_{tot} = \sqrt{S^2_{measurement} + S^2_{sample}}$$

The standard deviation of the value of the results in terms of the analyzed material is determined by the analyzers to a significant extent only if the variance for the sample preparation is markedly less than the variance of the analyzers. Therefore, the results are only reproducible if the sample to be analysed is fully representative of the material to be tested.

In this context, "representative" is generally understood to mean that the samples taken can be equated with the entire batch. If the mixture state of the original sample is described by a property function, the sampling is representative if the measured values distributed over the location adequately approximate the property function.

If a number of individual samples are taken from a well-mixed whole, its composition is subject to a statistic fluctuation insofar as a specific feature is concerned. An error can result because a sample is taken from a segregated basic quantity and always occurs in this case since mixtures are never ideal. To minimize the errors, as many small samples as possible must, therefore, be taken from random locations in the basic whole and then combined.

### The Solution:

Usually, the sample available to the laboratory may be 2000 g, whereas the quantity used for analysis is less than 200 mg. So, we have to have an accurate method of subdividing the lab sample so that the trial 200 mg used for analysis is fully representative of the original. This is the ideal situation and can only be achieved with an accurate sample divider. Whether division is in one or more steps has no relevancy over error preparation only on the costs of the additional cleaning processes.

The FRITSCH rotary cone sample divider LABORETTE 27 is, therefore, available with a division ratio of 1:30

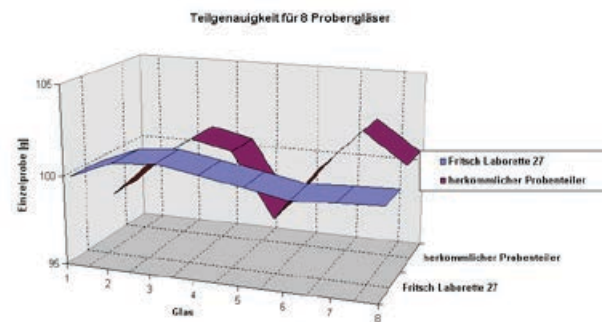


Figure 1: Sample Division with 8 Sample Containers

among others. This makes it possible to divide total samples of up to 300 ml into 30 individual samples in one step. Also, dividing cones with ratios of 1:8 or 1:10 are available in different materials so that they can be matched to different types of samples.

The patented design is based on the combination of 3 division methods within a single instrument. The sample is fed onto a dividing cone via a hopper. The dividing cone is de-signed to emulate the process of Coning & Quartering which is acknowledged as being the most accurate technique for sample division. The entire system rotates and the sample material is accelerated outwards so that it is transferred into the guide channels en-suring that as many as 30 individual samples are collected. The rotation of the dividing cone increases the number of divisions to up to 2,600 per minute, hence the ultimate sample is composed of a very large number of individual samples.

### The Results:

A mixture consisting of about 800 g of quartz sand was created and divided. Figure 1 compares the FRITSCH rotary cone sample divider with a rotary sample divider

with local feeding directly over the sample containers. To attain the same ratios, the dividing cone for eight 500 ml sample containers was used.

A check of equal division of samples to the sample containers showed that the LABORETTE 27 is clearly superior to conventional sample dividers.

Figure 2 shows no significant differences in the particle size distribution for each re-ceiver. The deviations per sample are very small. The analysis was conducted with the laser particle sizer FRITSCH ANALYSETTE 22.

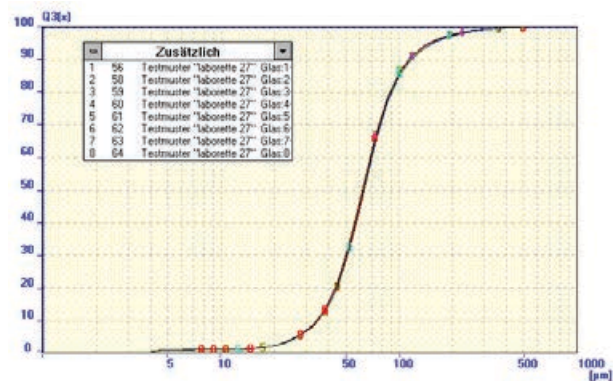


Figure 2: Particle Size Distribution

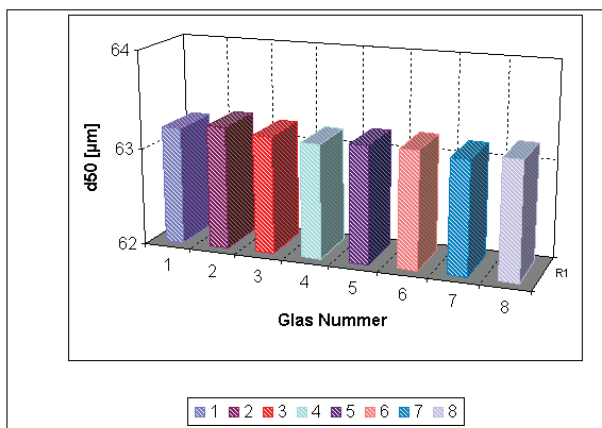


Figure 3: Median Values per (?)

The presentation of the d50 values (Fig. 3) shows that the median value of distribution in all sample containers is very well represented.

Figure 4 shows the median values of particle size distribution in the individual sample containers in series 1, whereas 8 reproducibility measurements of the same material are plotted in series 2 with no change in the instrument parameters.

The median average of the 8 reproducibility measurements is  $x = 63.1925 \pm 0.012$  [µm], whereas the median average of the individually measured samples in the 8 sample con-tainers is  $x = 63.1975 \pm 0.027$  [µm]. The comparison





illustrates that the accuracy of the analyzer is naturally considerably higher than the accuracy after sample division. Nevertheless, it is clearly evident that the systematic error caused by the LABORETTE 27 is very small indeed.

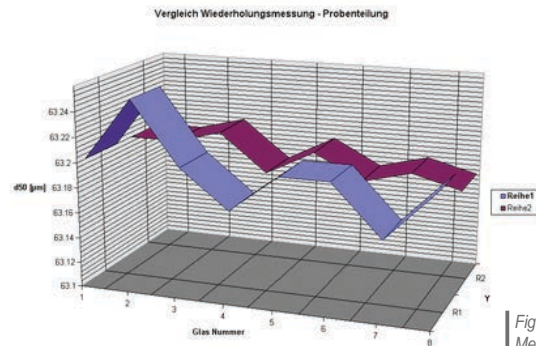


Figure 4: Comparison of Multiple Measurements with Sample Division

### Conclusions

The dividing accuracy exerts a decisive influence on the precision of a feature analysis. It can be minimized through design measures. FRITSCH succeeded here with the LABORETTE 27: this rotary cone sample divider enables modern analyzers to fully exploit their capabilities. The LABORETTE 27 should stand side-by-side with every modern analyzer.

# How OPTICAL SENSOR TECHNOLOGY SUPPORTS SUSTAINABILITY EFFORTS



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Businesses have launched sustainability initiatives to reduce their carbon footprint, minimize waste and encourage materials reuse and recycling. Here's how optical sensing technologies play a key role in these efforts. Inspired by a growing awareness of the consequences of climate change, an acknowledgement of the fragility of the environment and an anticipated scarcity of vital resources, companies from automakers to tech giants are taking steps to be more responsible corporate citizens. This movement echoes the changing attitudes of customers, who are rewarding companies that invest in sustainability efforts with their patronage and brand loyalty. Technology is a vital element of successful sustainability efforts, especially in resource management and recycling efforts. In this article, we will focus on the powerful optical sensing technologies that help industry to recycle metals, plastics and other materials more effectively.

## ***Technology and the Circular Economy***

There may be as many definitions of a circular economy as there are strategies to make such an economy viable. At its simplest, a circular economy incentivizes the reuse of products to prevent them from ending up in a landfill or polluting the environment. Circular economy models apply across every industry sector. Indeed, according to various industry and government reports, up to %60 of businesses today have sustainability strategies, with emissions reduction and sustainable (recyclable) products frequently cited as important pillars of those strategies. This is where

optical sensing strategies play a role in a) ensuring accurate sorting and processing of recyclable materials such as metals, glass and plastics, and b) analyzing the quality of new products that can be remade from those materials.

These techniques are non-destructive or minimally invasive, can be configured into instruments to make measurements rapidly, and are easily integrated into recycling operations. Although far from comprehensive, here are commonly used sensing technologies used in recycling processes:



Table 1. Commonly used sensing technologies used in recycling processes

Technique	Recyclable Materials	Use
Color measurement	Glass, Plastic, Metals	Separation or inspection by color
Machine vision	Metals, Plastics	Separation or inspection by color and shape
LIBS	Aluminum and Non-ferrous Metals, Glass	Sorting and identification by elemental analysis
NIR spectroscopy	Cardboard, Paper, Plastics	Sorting and identification by chemical composition (plastics), moisture content (cardboard, paper)
Raman spectroscopy	Plastics	Sorting and identification by chemical composition
X-ray	Metals	Sorting and identification by elemental analysis



### Metals Recycling

Metals are highly recyclable, with recyclers often using magnetics and X-ray spectroscopy as part of the initial sorting process. However, those technologies are unable to cleanly and efficiently separate out non-ferrous metals such as aluminum, magnesium and titanium. This is a significant obstacle for recyclers, who rely on efficient processes to achieve the optimum recycled output. That is now changing. Laser induced breakdown spectroscopy (LIBS) is a sensing technology that not only separates aluminum and magnesium, but also separates different aluminum alloys, or families.

Compared with other technologies for aluminum recycling, LIBS is more precise, eliminates a hazardous chlorination step currently used to reduce magnesium during recycling, and is less prone to breakdowns that can occur with other sorting systems. Consider that approximately %3 of the world's annual energy output goes toward making primary aluminum. By recycling aluminum and then remelting it in a secondary furnace to form new aluminum, energy savings of up to %95 are realized compared with producing primary aluminum. In addition, recycling minimizes or eliminates the mining of bauxite for primary aluminum, a process that consumes energy and can result in environmental concerns.

As a major user of metals, the automobile industry has a clear interest in diverse ways to conserve resources. Lighter vehicles save energy, which makes a strong yet lightweight metal like aluminum attractive. Also, with electric vehicles becoming more popular, there are metals including nickel, cobalt and lithium that will need to be detected and separated as market forces and environmental considerations related to primary metals will determine.



## Plastics Recycling

Plastics recycling is a multi-faceted area, with the aim of creating a circular plastic economy requiring major changes in how we design, recycle and reuse plastic products. There are several sustainability challenges related to plastics:

**Most Primary** plastics are made from petroleum products, which contribute to global emissions.

**The Prevalence** of single-use plastics contributes an inordinate amount of overall plastics waste.

**Very Little** used plastics have been recycled, with most ending up in landfills.

**The Variety** of plastics and differences within the chemical composition of similar families of plastics make it difficult to recycle plastics cost effectively.

**When Plastics** are sorted inaccurately, the resulting reprocessed version may be useable only as black plastic, effectively marking the end of that plastic's recyclability.

Let's narrow our focus on the issue of plastics sorting. The synthetic materials comprising some plastics use macromolecules such as polymers. These polymers are commonly manufactured through injection molding at low temperatures, suggesting that reuse of the materials via recycling is simple. However, very few types of plastics can be blended into homogeneous mixtures, which makes it necessary to cleanly separate the different polymers in the recycling stream.

Techniques including UV-visible spectroscopy, NIR spectroscopy and Raman analysis can provide useful information about plastic characteristics including color and chemical composition. For example, certain polymers have distinct NIR spectral features, which closely correlate to the recycling codes imprinted on plastics. Also, at sufficient signal levels and with adequate methods to mitigate interference from fluorescence,

Raman can be highly specific for plastics identification.

As effective as Raman and NIR spectroscopy are for clear and colored plastics identification, neither method is well suited for identification of black polymers. That's because carbon black absorbs Raman excitation laser light and light in the NIR region. Black plastics are not typically recycled and instead end up incinerated or in a landfill, although recent advances in sorting technologies could alleviate those outcomes.

In addition to these sensing techniques, as well as imaging technology like CCD cameras, recyclers can benefit from the emergence of more sophisticated data analysis algorithms, which can be applied to the spectral signature sorting data collected to group and classify the samples by type. Applied to an automated recycling sorting process, these algorithms provide another layer of insight into separating polymers more efficiently and with fewer errors.

## Recycled Product Quality

Improving and refining recycling processes is primarily focused on the sorting and classifying stages of the operation. Certainly, the effectiveness of the circular economy depends on how well -both technically and economically -that element of the system functions. But let's not overlook the quality of the remade materials. Does this aluminum meet the requirements of each alloy grade, which range from pure aluminum to aluminum with alloying elements including copper, manganese and zinc? What quality parameters for remade plastics will the market demand? Will there be new regulatory issues for remade products to consider? Optical sensing technologies can play a role addressing these questions too and it's encouraging to observe the rate of technology innovation and adoption with recycling industries.

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## COMPARISON OF HPLC and IC Methods For the Determination of Anions and Organic Acids in Plating Baths

### **Abstract:**

**Sensitive and Accurate** determination of organic acids, breakdown products and organic contamination in chemical baths, and in plating baths can be made

### **Introduction**

The quality of plated deposits primarily depends on many factors, for example, temperature, effective bath pH, current density, additives concentration, solution composition, solution agitation and speed (rpm for barrel plating or line speed for reel to reel) in the tank. Mechanical factors are important, but, tight control of additive concentrations and the main component in a plating bath is extremely important to achieve successful results. Plating component concentration must be controlled at the recommended limits, as suggested by the manufacturers. The bath components are monitored frequently to maintain concentration within a controlled window. Impurities of chemical additions and leaching of impurities are

using an ion chromatography and HPLC combined with size exclusion and post column reaction method. The advantages and cost of methods are evaluated and compared for finding the maximum efficiency.

added into the tanks. Wet chemical methods are used for monitoring bath components. Advanced automatic instrumentation is also available for the analysis of inorganic and organic species. Plating baths are usually analyzed offline after harvesting samples from various tanks. Metal ions are monitored using inductively coupled plasma (ICP), atomic absorption spectrophotometry (AA), polarography, wet titrations, and ion selective electrodes, colorimetry. The analytical methods for the analysis of plating solutions should be simple, direct, and operator friendly. Trace pollutants in solutions should be determined by a certified laboratory equipped with the desired instrumentation for micro-determinations. The workload of a plating plant can justify the use of any instrumental technique,



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such as AA, ICP, chromatographic techniques, or any dedicated electrochemical method.

Reversed-phase HPLC method is the most used separation mode. This mode is based on the hydrophobic interaction between the portion of the low polarity of the packing and the portion of the low polarity of the sample. Therefore, elution occurs in descending order of polarity. A key to successful organic acid analysis in reversed-phase mode resides in thoroughly suppressing the dissociation of organic acids and reducing the polarity of the sample. Organic acids are generally reported to become non-dissociated when the eluent has a pH value lower than the pKa by 1.5.

In anion exchange methods, the resin surface is positively charged. The cation on the resin is scrambled by the anion of the component mobile phase and the organic acid anion, so elution occurs

in ascending order of ionic absorptivity. Size Exclusion Mode Organic Acids are eluted in ascending order of molecular size. Molecules larger than the pore size of resin are eluted as the first peak. In Detection of Organic Acids, the functional group shared by organic acids is the carboxyl group, which has a UV absorption band between 200 and 210nm, thus enabling the use of a UV detector. However, because many other organic substances have the same wavelength band for UV absorption and the molar extinction coefficient is low at 50 to 70, the detection of organic acids is likely to be influenced by impurities. The RI detector lacks selectivity and remains somewhat problematic with regard to sensitivity. Detection using the conductivity detector (CD) is prone to sensitivity variation depending on the kind of organic acid. As a method of selectively detecting organic acids, the post-column method using a pH indicator is available which employs a visible absorption spectrum (VIS) detector.

### Instrumentation:

The following is needed for the anions and organic acid determination with HPLC and IC:

Mobile phase pump (S1130, isocratic or gradient), Derivatization pump (S1130, isocratic), S5300 Sample Injector, UV S3250, Post-column reactor, PCR with T-piece. All components are from Sykam Company. Pre-column and anion separation columns are from Shodex Company.

The determination conditions of organic acids with HPLC are shown in Table 1. Picture 1 demonstrates

the chromatogram of organic acids with HPLC in this condition.

Table 1: Analytical and Instrument Condition in Determination of Anions and Organic Acid with HPLC

Parameter Value	Parameter Value
Eluent	2 mM Perchloric Acid/CH <sub>3</sub> CN=10/90
Flow Rate (Eluent)	1.0 mL/min
Column Temp.	47
Technique	RP
Detector	VIS (430 nm) post column method
Injection Volume	20 µL

Table 2: Analytical and Instrument Condition in Determination of Organic Acid with IC

Analytical Conditions are shown in table 2 for anions and organic acid determination with IC. Picture 2 demonstrates the chromatogram of anions and organic acid with IC in this condition.

Parameter Value	Parameter Value
Eluent	6 mM Perchloric Acid
Flow Rate (Eluent)	1.0 mL/min
Column Temp.	50°C
Detector	Inverse Suppressed conductivity
Technique	Ion exclusion
Injection Volume	20 µL



### Experimental:

Mixture of Succinic acid, Lactic acid, Formic acid, Acetic acid, Propionic acid, Isobutyric acid, n-Butyric acid, Isovaleric acid and n-Valeric acid are determined in an organic compound applying ion-exclusion chromatography and conductivity detection after inverse suppression. For the inverse suppression, the Suppressor Module is used in its lithium form to reduce the background conductivity and to convert the

acids to their fully dissociated Li<sup>+</sup> form. Regeneration is performed by lithium chloride.

The solution includes Citric acid, Tartaric acid, Pyruvic acid, Malic acid, Succinic acid, Glycolic acid, Lactic acid, Fumaric acid, Acetic acid, Levulinic acid, Pyroglutamic acid, Propionic acid, Isobutyric acid, and n-Butyric acid are determined in reverse phase HPLC mode after post column reaction for improving the sensitivity and selectivity.

Table 3: Operation Concentration Range of Organic Acids in IC

Component	Operation Range [mg/L]
Organic acids	0.5 – 100

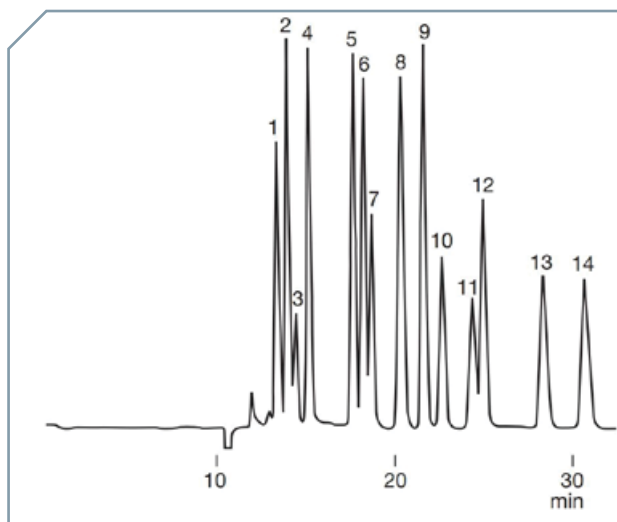
Table 4: Operation concentration range of organic acids in HPLC

Component	Operation Range [mg/L]
Organic acids	500 – 5000

### Conclusion

An aqueous mobile phase was used which comprised (created) a 0.002 molar HClO<sub>4</sub> in the aqueous phase and acetonitrile in an organic phase. Sulfuric acid also could be used as the mobile phase. Organic acid components could be determined by both of the methods with each one having its own advantages and disadvantages. Some of these properties, like sensitivity and resolution are obvious and shown in picture 1 and picture 2 as chromatogram of organic acids by two methods.

Also, different components of organic acid are shown in table 5 and table 6.



Picture 1: Chromatogram of Determination of Organic Acid with HPLC



Table 5: Organic Acid Components Concentration in HPLC Determination

Component	Concentration (ppm)	Component	Concentration (ppm)
1 Citric acid	500	8 Fumaric acid	500
2 Tartaric acid	500	9 Acetic acid	500
3 Pyruvic acid	500	10 Levulinic acid	500
4 Malic acid	500	11 Pyroglutamic acid	500
5 Succinic acid	500	12 Propionic acid	500
6 Glycolic acid	500	13 Isobutyric acid	500
7 Lactic acid	500	14 n-Butyric acid	500

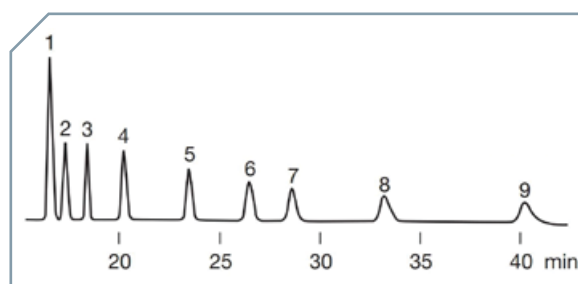




In addition, other inorganic anions are determined simultaneously with organic acids in the ion chromatography method. Some of these anions are chloride, carbonate, phosphate, etc.

In the IC method, if there is no need to post column reactor, then there is no need for an additional pump and chemicals for PCR, therefore it is more economical and cost effective.

Also, with ion chromatography, it is possible to determine components in a wide range, more sensitively and accurately.



Picture 2: Chromatogram of Determination of Organic Acid with IC

	Component	Concentration (ppm)
1	Succinic acid	10
2	Lactic acid	10
3	Formic acid	10
4	Acetic acid	10
5	Propionic acid	10
6	Isobutyric acid	10
7	n-Butyric acid	10
8	Isovaleric acid	10
9	n-Valeric acid	10

Table 6: Organic Acid Components Concentration in IC Determination

**Reference:**

- [1] Sykam instruction manual for HPLC and IC, 2022, S1130, S3250, S150
- [2] Kurt E., HeikkilaRodney K., WilliamsRussell J. Pylkki, 1985, US4628726A
- [3] Stuart A. Oehrle, Determination of inorganic and organic ions in nickel-plating baths by capillary electrophoresis, Journal of Chromatography A, Volume 739, Issues 1–2, 1996, Pages 413-419
- [4] Shodex HPLC column catalogue, 2022
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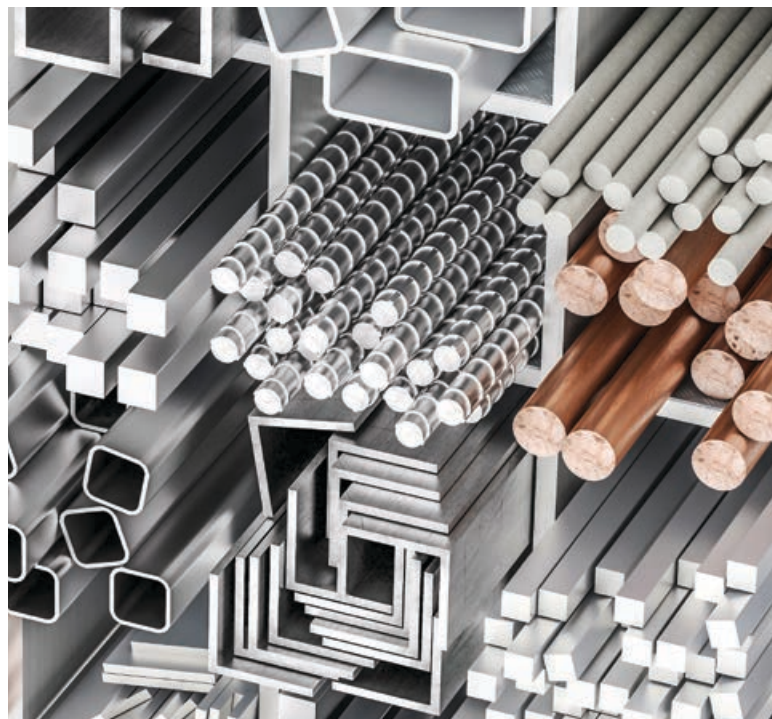
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## LIGHT-ELEMENT ANALYSIS in Metal Alloys-elements That Challenge Handheld XRF and Not Mobile Spark-OES

### *Introduction:*

Light element analysis with handheld x-ray fluorescence (XRF) is a big challenge because it depends on the ability of the detector to detect the fluorescent energies that are unique to each element. In turn, how far a fluorescent energy from each atom can travel depends on the strength of that discrete energy. The lighter the element or the lower its atomic number, the weaker its fluorescent energies and the shorter the distance they can travel. The elements that are known as light elements have such weak fluorescent energies that it is difficult for them to cover the distance between the sample surface and the detector in an air path; they lose their energy within a very short distance. Common solution to this problem is to create a vacuum purge or to use helium to purge the path between the sample surface and the detector. However, these constraints make it difficult or impossible to get satisfactory performance from handheld XRF in a number of applications. This section introduces challenging elements for handheld XRF and explains how they may instead be routinely analyzed by mobile spark-OES.



### Carbon:

Carbon content not only determines the strength and brittleness of steel in an application, but it affects how the metal can be worked. Because of difficulties with identifying elements lighter than Ti, handheld XRF lack the ability to determine the carbon (C) content of a metal sample. This makes these instruments unsuitable for reliable analysis of some metal alloys, including two common varieties of steel, namely low- alloy and Chromium/Nickel (CrNi) steels.

The amount of carbon present in a sample is the chief factor available for distinguishing between different low-alloy steels (sometimes called carbon steels). For applications from incoming/ outgoing inspection to repair, users often must discern small differences in elemental composition between grades. When processing low-alloy steels for use in engineering/ construction of structures, vessels, vehicles, or machines, weldability becomes a key characteristic. Steel alloys are weldable without special measures when they contain up to about %0.2 carbon. However, after that point, weldability decreases as carbon content increases.

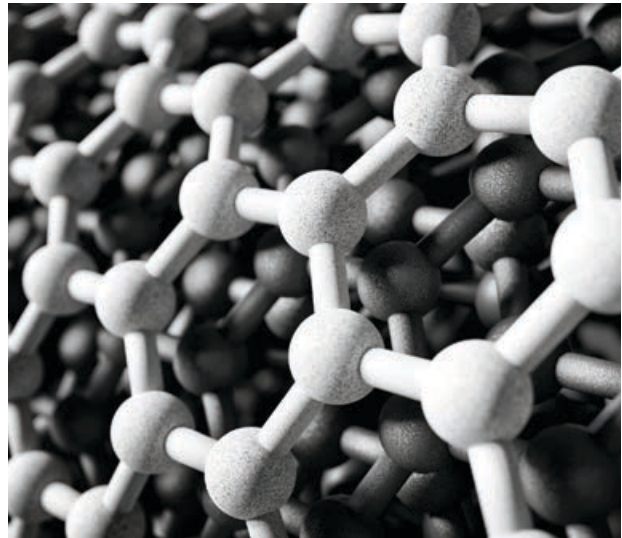
On the other hand, in CrNi steels, requirements for certain stainless or high-alloy steels demand precise analysis of carbon as well. For example, -Type 316 stainless steels are widely used in the construction of petrochemical plants. All 316 steel grades contain chromium; however, their mechanical strength and durability also depend on their carbon content. Type 316 stainless steels contain up to %0.07 carbon, while 316L stainless steels contain a maximum of %0.03 carbon. So, a small absolute difference of a few hundred parts per million (ppm) is enough to give these alloys clearly different intergranular corrosion behaviors. Welded seams formed in low-carbon 316L are more durable than in the higher-carbon alloy. Unlike handheld XRF, high-quality mobile or portable spark-OES spectrometers can easily differentiate these alloys on the spot.

### Carbon

Labels for the Carbon element card:

- atomic number: 6
- symbol: C
- electron configuration: [He]2s<sup>2</sup>2p<sup>2</sup>
- name: carbon
- atomic weight: [12.0096, 12.0116]
- acid-base properties of higher-valence oxides: Weakly acidic
- crystal structure: Hexagonal
- physical state at 20 °C (68 °F): Solid

Other nonmetals	Solid
Hexagonal	Weakly acidic



### Sulfur\*

atomic number	16	[32.059, 32.076]	atomic weight
symbol	S		acid-base properties of higher-valence oxides
electron configuration	[Ne]3s <sup>2</sup> 3p <sup>4</sup>		crystal structure
name	sulfur*		physical state at 20 °C (68 °F)

Other nonmetals	Solid
Orthorhombic	Strongly acidic

\*Also spelled sulphur.

### Phosphorus

atomic number	15	30.973762	atomic weight
symbol	P		acid-base properties of higher-valence oxides
electron configuration	[Ne]3s <sup>2</sup> 3p <sup>3</sup>		crystal structure
name	phosphorus		physical state at 20 °C (68 °F)

Other nonmetals	Solid
Cubic	Weakly acidic

### Sulfur and Phosphorus:

Sulfur (S) and phosphorus (P) are two other elements whose measurement is often critical to accurate metals analysis. Unfortunately, both are so-called light elements that are challenging for handheld XRF. So, for example, XRF analyzers can only identify metal grades with quite high sulfur values, such as Type 303 steel, which contains a minimum of %0.15 sulfur.

By contrast, Type 304 or 316 CrNi steels have a maximum of %0.03 sulfur. Such low concentrations cannot be reliably detected by handheld XRF analyzers. Their limits of detection (LODs) are usually too high to determine critical in-spec and out-of-spec levels in CrNi steels typically less than %0.03 sulfur. Similar problems arise with low concentrations of phosphorus. The necessary measurements are likely to be at or near a handheld XRF analyzer's basic limits of precision. They may also be thrown off by the impact of surface preparation anomalies in any given sample.



### Aluminum, Silicon, and Magnesium:

XRF technology also encounters problems when trying to measure aluminum (Al), silicon (Si), and magnesium (Mg) elements in metals. Again, the cause is inherently high LODs. Handheld XRF analyzers may often be able to identify these elements at lower levels. But, especially at levels below %0.1, they typically cannot reliably analyze them. For example, in many aluminum-based metal samples, magnesium measurement becomes critical. An advanced handheld XRF analyzer is able to detect Mg concentrations that let it differentiate among samples of 2000 or 6000 series Al-alloys. But, no handheld XRF instrument can differentiate unalloyed or low-alloy 1000 series samples by Mg. Nor can it easily deal with poor sample surfaces in alloys with Al, Si, or Mg.

#### Aluminum\*

atomic number	13	26.9815384	atomic weight
symbol	Al		acid-base properties of higher-valence oxides
electron configuration	[Ne]3s <sup>2</sup> 3p <sup>1</sup>		crystal structure
name	aluminum*		physical state at 20 °C (68 °F)

Other metals	Solid
Face-centred cubic	Equal relative strength

\*Also spelled aluminium.

#### Silicon

atomic number	14	[28.084, 28.086]	atomic weight
symbol	Si		acid-base properties of higher-valence oxides
electron configuration	[Ne]3s <sup>2</sup> 3p <sup>2</sup>		crystal structure
name	silicon		physical state at 20 °C (68 °F)

Other nonmetals	Solid
Diamond	Equal relative strength

#### Magnesium

atomic number	12	[24.304, 24.307]	atomic weight
symbol	Mg		acid-base properties of higher-valence oxides
electron configuration	[Ne]3s <sup>2</sup>		crystal structure
name	magnesium		physical state at 20 °C (68 °F)

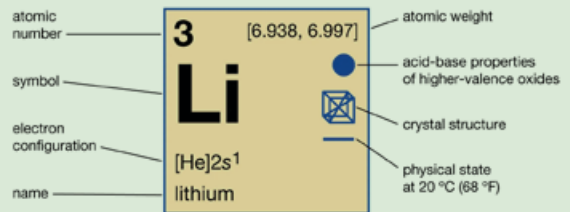
Alkaline-earth metals	Solid
Hexagonal	Strongly basic



**Lithium:**

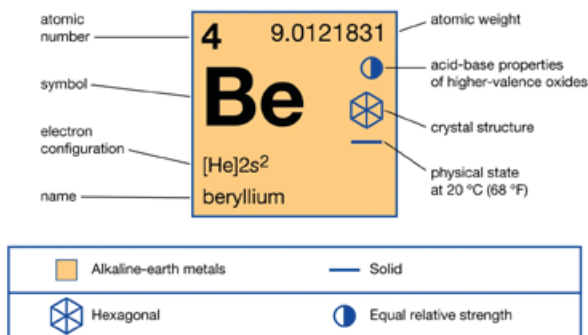
The lightest metal, lithium (Li) is frequently found in Al-based alloys. Up to a point, adding Li decreases weight without affecting strength. So, alloys, such as the 8090 series with %2.2 to %2.7 Li, are widely used in aerospace manufacturing, for example, where accurate analysis is required in incoming and outgoing inspection. Also, in metals recycling, it is vital to separate out Li-bearing alloys. Li reduces the ductility of standard Al-alloys with which it might be intermixed more than 5 ppm lithium content can cause difficulties in casting a recycled aluminum alloy.

**Lithium**



Alkali metals	Solid
Body-centred cubic	Strongly basic

### Beryllium



identify any Be content in a copper piece undergoing grinding, so that precautions can be taken to prevent exposure via skin or lungs. Unfortunately, Be is yet another element that is impossible to measure effectively with handheld XRF spectrometers.

### Boron:

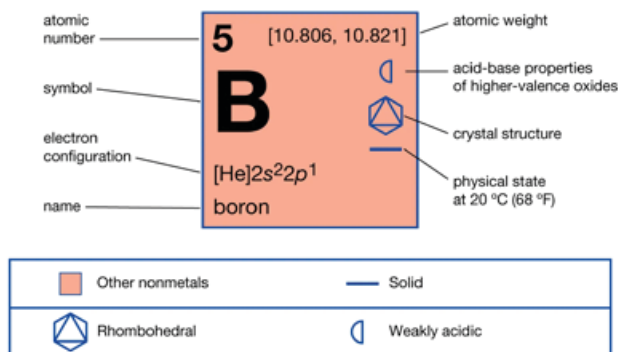
The basic effect of alloying with boron (B) is to enhance the hardenability of low-alloy steels. For example, the presence of B is key to distinguishing 13MnCrB5 from non-boron-bearing 16MnCr5 steel. Boron, also, helps high-speed blade steels improve cutting performance. Analysis can be critical for users, such as repair shops, which must determine the exact components of tool steels to effect repairs. In austenitic steels, low concentrations of boron (up to %0.01) improve the high-temperature strength of the finished alloy. These steels are used as construction steels, and for screws and fasteners. Once again, though, it is not possible to analyze boron effectively with handheld XRF technology.

### Beryllium:

Copper/beryllium (CuBe) alloys typically contain %0.4 to %2 Be in combination with cobalt (Co), chromium (Cr), or silicon (Si). They may be shaped into semi-finished bars, rods, etc., for further processing or used in valve seat rings or machine inserts, in nonarcing tools (for potentially explosive environments), and as die material for brass castings.

Awareness of Be content is also a safety measure. Be is among the chemical elements most toxic to humans. So, repair shops, for instance, must carefully

### Boron



### Conclusion:

All the elements mentioned in this report present significant challenges to measurement by handheld XRF analyzers. In several cases, handheld XRF techniques simply cannot detect them at all. Fortunately, recent advances in technology have created a new generation of high-capability, mobile and portable OES metal analyzers. They can quickly and precisely measure these challenging elements, or supply fast alloy sorting based on elemental content on the dock or at the line. Thus, in many applications where XRF technology just cannot deliver adequate performance, these mobile OES solutions have become the spectrometers of choice.

### Reference:

- [1] <https://www.spectro.com/products/mobile-metal-analyzer>
- [2] <https://www.thermofisher.com/Optical Emission Spectrometry Academy>
- [3] <https://www.portaspecs.com/why-light-elements-are-difficult-to-measure-with-portable-xrf/>



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## DIFFERENT ELEMENTAL ANALYSIS TECHNIQUES for the Characterization of Metal Alloys – Comparison

### **Introduction:**

**BETTER QUALITY** control for alloy manufacturing and sorting of post-consumer scraps relies heavily on the accurate determination of their chemical composition. Here, a study was conducted on the evaluation of four analytical techniques (energy-dispersive XRF, wavelength-dispersive XRF, LIBS, and spark-OES) for the determination of metal sample composition. It focuses on the quantitative analysis of nine commercial alloys, representing the three most important alloy classes: copper, aluminum, and steel.

### **Introduction**

One of the main obstacles for cost- and energy-efficient metal recycling is the contamination of post-consumer scraps with several metal impurities. In this case, the re-smelting of the scrap to produce a new target alloy within certain elemental concentration limits is only possible by adding primary raw material in the smelting process. To avoid this so-called downcycling effect, the contaminations in the post-consumer scraps need to be identified and treated separately. The accurate identification of modern, mixed waste fractions, containing impurities of a variety of metals in % to ppm-range, is challenging for most of the state-of-the-art analysis techniques but essential for closing loops in current metal production chains.

The present study focuses on the investigation of commercially available metal alloys, which can be regarded as representative for production scrap. First,

we compare our LIBS, EDXRF, and WDXRF results for the test alloys with unknown chemical composition to a more accurate dataset. Although spark-OES is accepted as a widely employed, reliable, and accurate technique for the quantification of metal alloys, this has to be proven by performing measurement with our spark-OES systems on samples with certified chemistry. Thus, we will demonstrate by the use of certified reference materials (in our case certified reference alloys-CRA) that spark-OES is a suitable validation method, against which the results from our LIBS, EDXRF, and WDXRF experiments can be benchmarked. Second, the results of statistical tests are presented, which were conducted to determine the spatial homogeneity. Finally, the results from LIBS, EDXRF, and WDXRF experiments with nine different test alloys are compared and discussed. The nine alloys belong to the three main metal matrices being produced by the metal industry: Al alloys, Cu alloys, and steels.



### Experimental

Nine certified reference alloys (CRAs) were used, comprised of three steel samples (ZRM 1-192, ZRM 3-284, ZRM 1-297), three Al alloys (EB 313, BAM311-, EB 315a), and three Cu alloys (BAM367-, BAM378-, BAM394-a). They are solid cylindrical blocks with

a diameter of 50 mm and a height of 20 mm. Their surfaces are flat-cut, but not polished to be comparable to the state of the test alloy surfaces.

For the comparison of the analytical techniques, nine commercially available alloys ('test alloys') were acquired, which are widely used in industrial applications (Table 1).

Table 1: Used test alloys with common abbreviations indicating quantities of their main elements

Alloy Name	Material Number	Main Applications	Analytical Challenge
Al99.5	AW 1050 A	Machining, plant construction	Low content of minor elements
AlMg4.5Mn	AW 5083	Shipbuilding, pressure vessels	Mixture of light elements Al and Mg
AlSi1MgMn	AW 6082	Food industry, packaging	Mixture of light elements Al, Mg, and Si
CuNi10Fe1Mn	CW 352H	Water pipes, capacitors	Mixture of several transition metals
CuZn39Pb3	CW 614N	Tool manufacturing, electronics	Accurate detection of heavy elements
CuSn8	CW 453K	Spring, pin connectors	Accurate detection of heavy elements
X5CrNi10-18	1.4301	Building material, sanitation	Detection of multi-element composition
45NiCrMo	1.2767	Tool manufacturing, plastic forming	Low content of minor elements
42CrMo4	1.7225	Automotive, mechanical engineering	Penetration of rusty surface





The test alloys were chosen in order to represent a large variety of chemical compositions, especially ones that are linked to a certain measurement problem. For example, two Al alloys, AlMg4.5Mn and AlSi1MgMn, contain aluminum and other light elements, such as magnesium and silicon, as well. These elemental mixtures are reported to pose difficulties for correct quantification by XRF analyses (Figure 1).

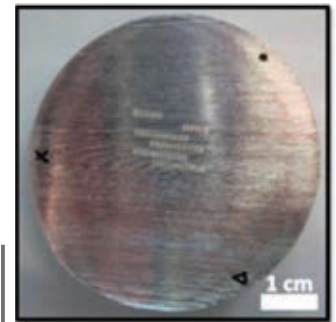
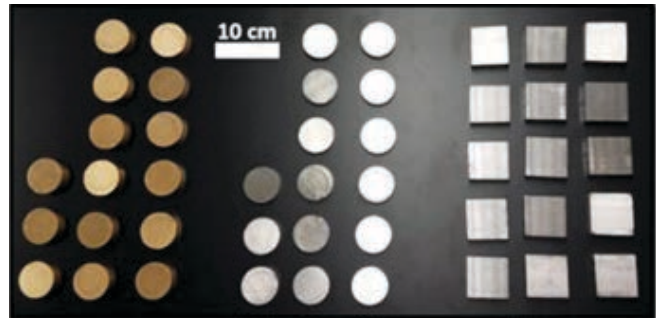


Figure 1: Photos of samples from three different classes of test alloys (left) after cutting and an exemplary piece after the measurements (right)

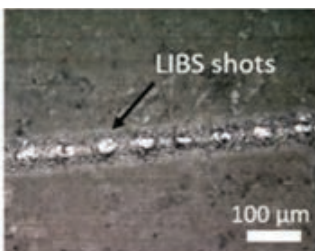
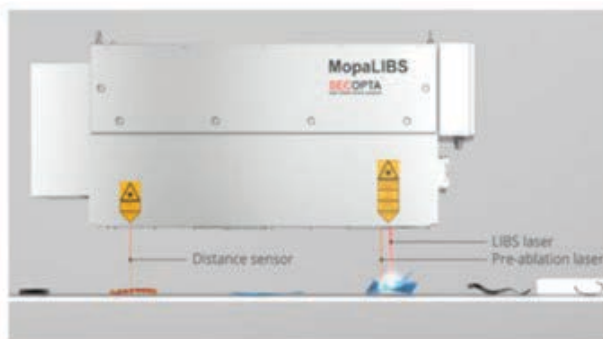


Figure 2. Schematic drawing of the used MopaLIBS device above a conveyor belt (left) - Both the LIBS laser and the pre-ablation laser are located behind the distance sensor. The movement direction of the belt is from the left to the right side of the image. Microscopic picture of the trace from the pre-ablation laser and shots from the LIBS laser (right).

Four different analysis methods were employed: EDXRF, WDXRF, LIBS, and spark-OES. Spark-OES has been used for benchmarking the results from LIBS, WDXRF, and EDXRF. For the analysis of the Al alloys, a spark-OES device ARL 4460 (Thermo Fisher Scientific, USA) was used. In addition, a Foundry-Master UV spark-OES device (Hitachi High-Tech GmbH, Germany) device was used for steel matrices. For the determination of the Cu alloy compositions, a spark-OES device Spectro Maxx F CCD (Spectro Analytical Instruments, Germany) was used. For the EDXRF experiments, an S1 Titan 600 model (Bruker, USA). For the WDXRF analysis of the test alloys, the measurements were performed using an AxiosMAX (PANalytical, The Netherlands). For the LIBS analysis of the test alloys, the measurements were performed with the MopaLIBS system (Figure 2) and LIBS Software Suite (Secopta analytics GmbH, Germany). For the measurements and analysis, the integrated application module Mopa Fast was used. The MopaLIBS which was installed over a conveyor and the system has a distance sensor to obtain a height profile of the scrap, a cleaning laser, and a LIBS laser.



In this system, a matrix-specific calibration for aluminum alloys and steels exists, but unfortunately no calibration for Cu alloys. Accordingly, only the three steels and the three Al test alloys were measured with this LIBS device.

### **Results and Discussion**

The results of the preliminary spark-OES experiments on the certified reference materials showed that we can use it as a benchmarking method for the other investigated techniques. The homogeneity test by EDXRF proved that our approach of using non-referenced alloys for the comparison of analytical techniques is valid because, apart from a few exceptions (e.g., steels 42CrMo4 and X5CrNi10-18), these alloys with known concentration limits are sufficiently homogeneous. Especially for the case of Cu, Si, Ni, and Mo in the steels, we attribute the inhomogeneities to problems in the manufacturing process. The influence of the employed cutting saw,

the only device that was in contact with the sample surfaces, can be excluded because no similar impurities were detected in the other alloys. Thus, we can compare various techniques with different measurement spot sizes for their accuracy in the quantification of the alloy compositions.

For most cases, the deviations of EDXRF, WDXRF, and LIBS from the values of spark-OES were rather small, indicating a suitability of all methods for the detection of major and most minor elements. Only a few exceptions are observed where one or more methods cannot detect a specific element in a specific alloy matrix properly. Whereas the absolute deviations of the EDXRF, WDXRF, and LIBS results from the spark-OES benchmark are in the low wt.%-range, relative deviations of higher than %100 of the measured spark-OES value occur. This held especially true for the low concentration range below 1 wt.%, where the effect of the precision for each method plays a strong role and directly affects the detection limit of the method.

In addition, the precision of the instrument influences the performance of the detection as well. That is why much attention has to be paid to the proper calibration of the targeted concentration range within a specific matrix (e.g., Ni in high-alloyed steels). If the response of the instrument to the analyte concentration is not linear anymore, false quantifications of unknown samples are produced during the routine analysis. The tolerable deviation for the selected analysis technique depends on the nature of the target element and the application for which the target alloy has to be produced or sorted. For example, if a low-alloyed steel, such as 42CrMo4 is produced and has to be assured that it conforms to the European specification, its silicon concentration has to be below 0.4 wt.%. If the manufacturer or recycler uses a commercially available portable EDXRF device, the test can fail, and a limit-exceeding Si content is observed. Thus, lower quality of the manufactured alloy is assumed which can limit the use to fewer applications and result in a remarkably (for this example, up to %50) lower selling price of the product.



By choosing LIBS or WDXRF for analysis instead, a standard conformity is obtained, leading to a categorization of the produced alloy as 42CrMo4, with potential use in automotive applications. The selection of the appropriate technique to analyze is fundamental for accurate quality control and efficient sorting process.

For the analysis of light elements in light element matrices (e.g., Mg, Al, Si in Al alloys), LIBS experiments show a better performance compared to the X-ray techniques. This is in accordance with the findings of previous studies, which is demonstrated for handheld analyzers. The X-ray cross-sections for the light weight elements Mg, Al, and Si are comparatively low comprised of an obstacle for a correct quantification by XRF. In addition, strong X-ray absorption by air and the polymer detector window diminish the received fluorescence intensity further. In comparison, LIBS ensures a more accurate analysis of these light elements and can, after proper calibration, also distinguish between individual classes of aluminum alloys, such as 5.xxx and 6.xxx. Remarkably, the LIBS results fit generally well to the spark-OES values, although the acquisition time (few ms) for this technique was the lowest of all used ones.

Similar to spark-OES, LIBS can create high signal counts in a short time by intense excitation pulses. Nevertheless, the experiments also showed that LIBS deviates in some matrices noticeably, e.g., more than %35 relative to the spark-OES value for the high-alloyed steel. The reason for this remains unclear but could be attributed to a non-sufficient base of calibration samples in the respective concentration range. Furthermore, we used lower acquisition times for the LIBS experiments than for the spark-OES measurements, resulting in a reduced signal-to-noise ratio and a potentially less accurate analysis.

Contamination of steels with copper, even a Cu content below 1 wt.%, is usually unwanted in certain steels because it can only be used in construction materials. Such a loss of variability of use leads to a downcycling for the original steel alloy and to an obstacle for an efficient circular economy of metals. As the results demonstrate, all employed analysis techniques are able to detect these impurities, allowing them for the use in quality control both for recyclers and metal-producers. Here, the XRF methods obtained more accurate results

than LIBS, caused by the comparably good X-ray cross-section and differentiability of Cu and Fe.

Besides the accurate quantification of the alloy composition, other operational-relevant parameters are also important for the evaluation of the performance of each individual analysis technique. A method, allowing for high throughput by an in-line analysis, can be much more economical, if it still shows a reduced, but satisfactory accuracy adequate to the analytical task. Especially LIBS is used in conveyor belt systems, running at belt speeds of a few meters per second. Therefore, the whole measurement process must be on a time scale of a few hundred microseconds. Contrary, the XRF techniques need acquisition times of several seconds to minutes due to their lower signal count rate and, for WDXRF, the consecutively scanning of each individual element-specific detection angle to obtain a complete spectrum.



A further important aspect is the effort needed for the calibration and operation of the method. As we experienced, the number of calibration samples required for an accurate multi-metal LIBS or OES calibration is much higher than the amount of reference materials needed for an XRF analysis. Most probably, this can be attributed to the more complex physical processes of plasma generation, ablation, and relaxation, resulting in a manifold of emission lines (especially for steels). However, a better performance of a well-calibrated system can also justify the higher effort for establishing the calibration and the operation of the analysis technique, if an accurate determination of traces of contaminations is needed. This can only be balanced by an economical assessment tailored individually to the specific analysis/separation task, for example, the correct determination of Mg in an Al alloy to decide to which alloy class the scrap piece belongs. Furthermore, several national and international standards exist instructing about the correct application of specific analyte preparation and analysis techniques for certain metal alloys and scraps. These are especially important for licensed laboratories and analysis departments of large recyclers but difficult to meet by non-optimized analysis systems and procedures in smaller recycling companies.

Regarding the alteration of the sample by the probing technique, clear differences between the X-ray methods and the OES methods can be seen. Whereas the first ones leave the metallic samples unaltered, the latter ones ablate the uppermost layers of the sample. The depth of the trace from the pre-ablation and LIBS laser depends on the material properties, laser properties, and velocity of the conveyer belt, ranging in our case from 20 to 40  $\mu\text{m}$ . With higher repetitions rates of the laser and lower speed of the conveyer

belt, the depth increases. The surface damaging penetration of the OES techniques has the advantage to probe a fresh surface, which is especially useful for the investigation of surface-coated alloys, such as low-alloyed/rusty steels or galvanized Al alloys. An effective way of probing the three-dimensional averaged composition or test for impurities in depth of several millimeters are none of the studied methods. Potential alternative future approaches overcoming some of these limitations could be the prompt gamma neutron activation analysis (PGNAA) or the spectrally-resolved X-ray computed tomography (XCT).

The results presented for the nine different, relatively pure (not oxidized nor mixed with other alloys) and homogeneous test alloys can be linked to the examination of production (or prompt) scraps, whose compositions are known to some extent prior to analysis. They are not yet mixed with other scrap streams. Such production scraps are already analyzed by multifold sensors to a satisfactory level in the metal industry and can already be sorted with high efficiency. As discussed above, there exists no single analysis technique, enabling a fast, easy-to-handle, and accurate composition determination in all-metal alloy matrices. One promising path to meet these requirements is the intelligent combination of several different methods in one analysis workflow/system. Several such multi-sensor systems for the in-line analysis and sorting of scraps have been successfully introduced in the past (years). Nonetheless, mixed post-consumer scraps still remain a major challenge due to their oxidized/dusty surfaces and their complex multi-alloy composition. The evaluation of the suitability of the WDXRF, EDXRF, LIBS, and spark-OES is subject to a study, which is currently being carried out.

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## DETERMINATION OF HEXVALENT CHROMIUM As an Environmental Pollutant in Metal Industries

**Abstract:**

**In the Past Years**, the use of chromium (Cr) in several industrial activities and the resulting contamination have increased environmental concerns. There are several oxidation states of Cr, but the most stable and common forms are Cr (0), Cr (III) and Cr (VI) species. The most toxic species of Cr oxidation state is Cr (VI), while Cr (III) is less toxic than other species. Plants soak up Cr through absorption of essential elements from soil and water. Different species of Cr cause differences

in uptake, accumulation and translocation, which also condition its toxicity to plants. Symptoms of Cr toxicity in plants are diverse and include a reduction of growth, seed germination, inhibition of enzymatic activities and nutrient and oxidative imbalances. They also cause a decrease in yield, impairment of photosynthesis and mutagenesis.

This analytical method describes the determination of the mean concentration of hexavalent chromium in surface water and metal industrial waste water.

**Introduction:**

Chromium plating is a technique of electroplating a thin layer of chromium onto a metal object. The chromium layer can be decorative, provide corrosion resistance, facilitate cleaning, or increase surface hardness. Chromium compounds used in electroplating are toxic, because they are the human carcinogens. In most countries, their disposal in mining and plating metal industries is tightly regulated.

Hexavalent chromium can be measured sensitively with photometric detection using post derivatization. Analytical separation is done on an exchanger, and an ammonium sulfate solution hexavalent chromium is derivatized by mixing the mobile phase with sulfuric acid.



**Instrumentation:**

The following is needed for the hexavalent chromium determination with photometric detection:

Mobile phase pump (S1130, isocratic or gradient), Derivatization pump (S1130, isocratic), S5300 Sample Injector, UV S3250, Post-column reactor PAR with T-piece, A01 pre-column and Anion separation column A01. All components are from Sykam Chromatography Company.



Table 1: Analytical and Instrument Condition in Determination of Hexavalent Chromium

Parameter Value	Parameter Value
Eluent	Eluent 250 mM Ammonium sulfate 100 mM Ammonia
Flow Rate (Eluent)	1.0 mL/min
Derivatization Reagent	1N H <sub>2</sub> SO <sub>4</sub> 2 mM -1,5Diphenylcarbazide (DPC) 10 % MeOH
Flow Rate (Derivatization Reagent)	0,7 mL/min
Column Temperature	ambient temperature
Post-column reactor PAR	100 cm, I.D. 1.6 × 0.5 mm
Post-column reactor temperature	ambient temperature
Injection Volume	100 µL

Analytical conditions are shown in table 1 for hexavalent chromium determination. Picture 1 demonstrates the chromatogram of Cr (VI) in this condition

**Experimental:**

In hexavalent chromium analysis, the calibration points are linear to the range of one decade. Nevertheless, it is not recommended to use a single point calibration. For wider concentration ranges, more calibration points could be necessary. In the case of non-linear calibration curves, it is recommended to divide the calibration range in separate calibration curves. The following

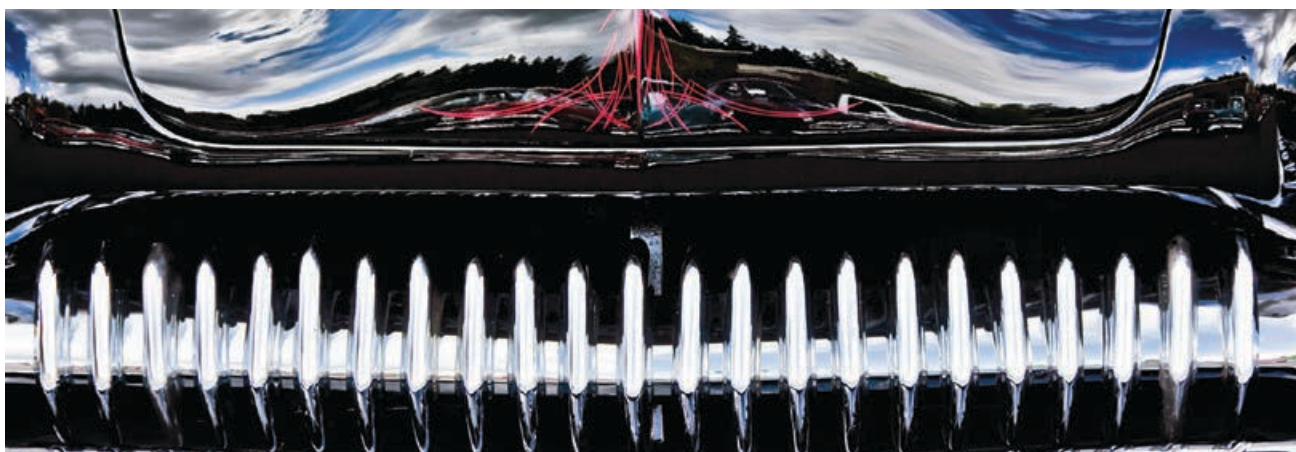
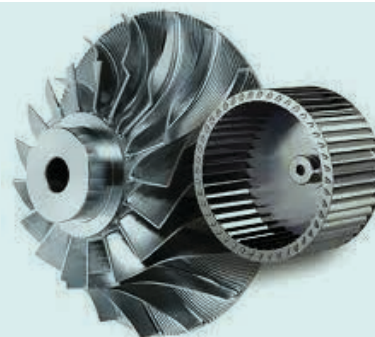
operation range results from a measuring range of 200 to 1000 µAu with an injection volume of 100 µL and with a calibration (linear curve with zero intercept) carried out with the standard listed in table 2.

Table 2: Standard Calibration Range of Chromium

Component	Operation Range [µg/L]
Chromium (Cr <sup>6+</sup> )	5,0 – 0.5

Table 3: Calibration Standard Concentration For Determination of Hexavalent Chromium

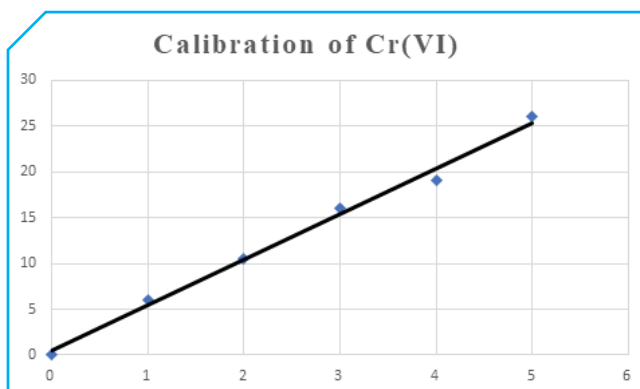
Component	Blank [mg/L]	C <sub>Std.1</sub> [µg/L]	C <sub>Std.2</sub> [µg/L]	C <sub>Std.3</sub> [µg/L]	C <sub>Std.4</sub> [µg/L]	C <sub>Std.5</sub> [µg/L]
hexavalent Chromium	0	1.0	2.0	3	4.0	5.0



## Conclusion

Calibration Standards Were Injected and a Calibration Curve Was Plotted in Picture 2

Picture 2: Calibration Curve For Hexavalent Chromium



Some parameters influence analysis and selectivity of Cr (VI) which are described below.

### Flow Rate

The flow rate has a proportional effect on the ion's retention time. That means, the higher the flow rate, the shorter the retention time. Higher flow rates, however, cause higher back pressure and consequently shorten the life span of the column. A flow rate of 1.0 mL/min should be used with the anion separation column.

### Temperature

Due to improved ion exchange processes, an increasing column temperature above °30C leads to slightly higher retention times for the hexavalent chromium. This method works (can be safely used) at ambient temperature.

The A01 separation column is limited to °60C. Using higher temperatures will damage the column.

### Influence of pH-value

Due to the chromate dichromate equilibrium, the pH value of the mobile phase has an influence on the

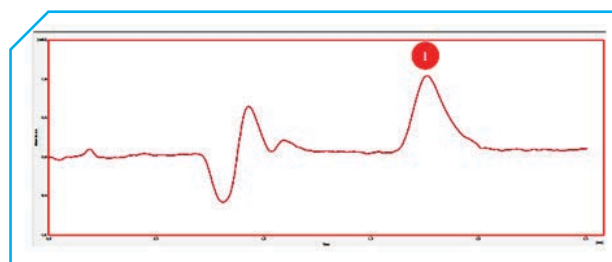
chromatography. Hence, the recommended mobile phase composition must be strictly adhered to.

### Column life time

The longer column is in use, the faster ions will elute (capacity decrease) resulting in a slight shift (reduction) of the retention time and a bad peak shape.

### Deionized Water

The use of ion-reduced (free) water for cleaning labware and prepare eluents, calibrators and blank samples is important, especially when measuring at low ion concentration levels. Therefore, it is recommended to use deionized water (<1 µS/cm).



Picture 1: chromatogram of Cr (VI) with described condition

## Reference:

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- [2] Chagas, P.M.B., Caetano, A.A., Tireli, A.A. et al. Use of an Environmental Pollutant From Hexavalent Chromium Removal as a Green Catalyst in The Fenton Process. Sci Rep 9, 12819 (2019)
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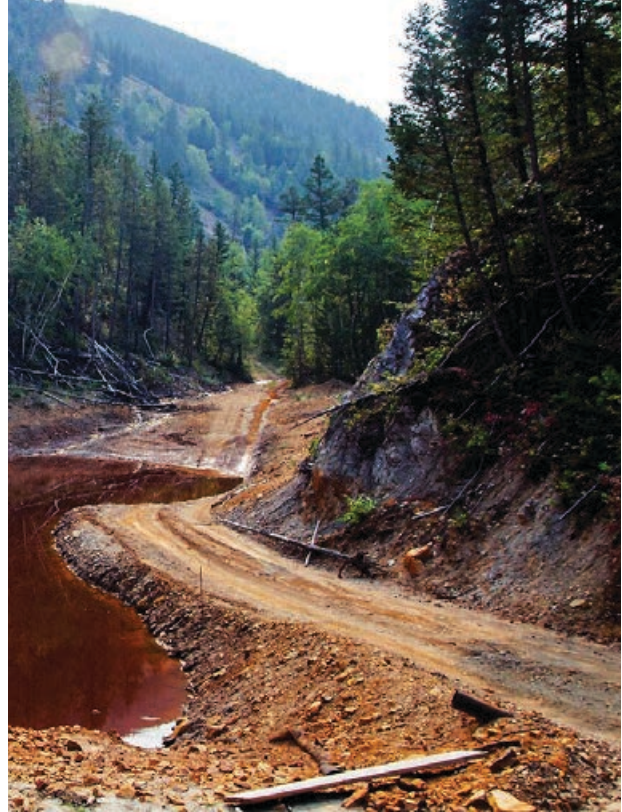
## DETERMINATION OF GOLD by Stripping Voltammetry on Modified Electrode

### **Abstract:**

**THIS PAPER** describes the method for determining the gold (III) by stripping voltammetry on graphite modified electrodes. The results show that modification by this method increases the sensitivity (precision) of the detection of gold by 2 times.

**Introduction**  
The universal tendency is to use

objects with a poorer and more complex composition of ores and gold content is much lower than in the feedstock [1]. Such materials are poor, finely disseminated, arsenical ores and ores of small deposits, old tails to gold enrichment plants. For determining gold trace in these kinds of ores samples, the stripping voltammetry has been used for a long time.



### Experimental

The samples were dried to a constant weight and dispersed onto a flat surface. A sample was taken from the combined sample using an analytical balance. The weighed sample was placed in a corundum crucible and then, placed in a furnace. The furnace temperature was raised and held for a time. The muffle furnace was disabled, and the sample was cooled to room temperature. Then concentrated HF was added to the sample and evaporated on a hot plate to a dry residue. Then aqua regia was added to the sample and heated for a certain amount of time. HCl was added to the resulting solution, and then the solution was cooled and filtered it. The precipitate was washed with distilled water. The residuals were transferred to a funnel, and Diethyl ether was added, and gold (III) extraction was carried out twice. The washed ether was cast into a quartz beaker and evaporated with gentle heating until a wet cake condition. After that, 6M HCl was added to the solution and evaporated to a minimum sample. The solution volume was made up to 10 ml with bi-distilled water and the content of gold (III) was determined by the stripping voltammetry method. The electrochemical cell consisted of a 3- electrode, wherein the indicator electrode is a graphite electrode (GE) impregnated by polyethylene. Removal of the electrode surface from gold precipitation was carried out for 1 minute with a potential of +1.0V. Platinum wire and Ag/AgCl electrodes were used as the subsidiary electrode and the reference electrode.

### Results

The calibration curve dependence on the determination of gold ions (III) by stripping voltammetry using graphite electrode without a modifier and modified graphite electrode (Fig.1).

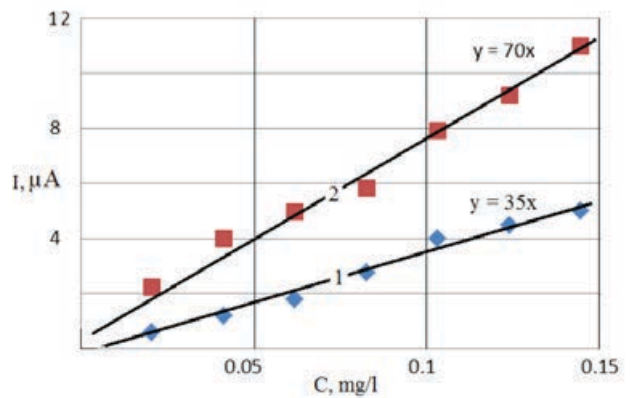


Figure 1. Current-voltage curves of electrooxidation Pd-Au precipitate from the graphite electrode surface. C, mg/d3: (1)  $C(\text{Au}^{3+})=1 \cdot 10^{-2}$ ; (2)  $C(\text{Au}^{3+})=1 \cdot 10^{-2}$  and  $C(\text{Pd}^{2+})=1 \cdot 10^{-2}$ ; (3)  $C(\text{Au}^{3+})=1 \cdot 10^{-2}$  and  $C(\text{Pd}^{2+})=2 \cdot 10^{-2}$ ; (4)  $C(\text{Au}^{3+})=1 \cdot 10^{-2}$  and  $C(\text{Pd}^{2+})=3 \cdot 10^{-2}$ .



As the results show, GE modification increases the sensitivity of the gold (III) determination two times.

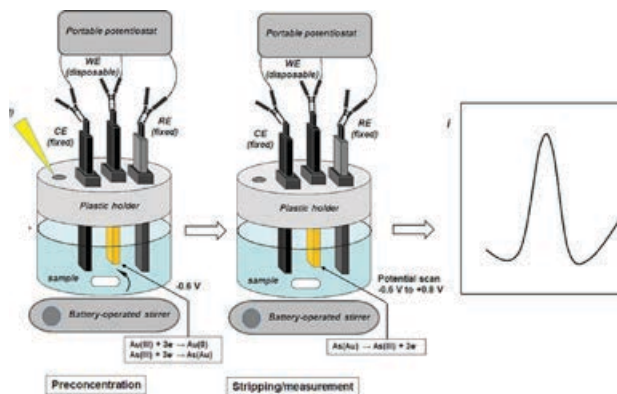


Figure 2. Calibration curve of gold detection from ion concentration of gold (III) in a solution: 1- currents of gold detection from the surface of the graphite electrode; 2- currents of gold detection from the surface of the graphite electrode modified by bismuth

A comparison of the results in gold determination by stripping voltammetry and atomic absorption spectroscopy method shows the equivalence of the two methods as the absolute value of concentration and determination error [2]. However, the cost of analysis is reasonable due to the simplicity and low-cost equipment in comparison to other methods.

According to this paper, the below points should be mentioned:

- 1- Stripping voltammetry method using bismuth-graphite electrode selective for gold allows the analysis of gold in a wide range of interfering impurities.
- 2- Modification of graphite electrode using bismuth improves lower concentration limits for gold 2 times.
- 3- Stripping voltammetry method is comparable in quality, error determination, and rapidity with atomic absorption and atomic emission method.

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## Detection of Multiple Heavy Metals by Stripping Voltammetry Using SPE

### **Abstract:**

**IN ANALYTICAL** laboratories, quantitative analysis is an everyday task. Monitoring processes and product quality are common tasks for electrochemical analysis. With the knowledge of pollution, monitoring heavy metals in water reservoirs, pipes, rivers, etc. is becoming more and more critical. Heavy metals are worthy of electrochemical detection; even trace concentrations can be measured.

### **Introduction**

Heavy metal ions are one of the main sources of water impurities. The issues of heavy metals contamination of local, regional, and global environment emanate directly from natural sources and indirectly from anthropogenic activities such as mining, rapid industrialization, urbanization, improper waste management, and other local and regional man-made activities. Most of them are carcinogens that threaten ecological balance and human health. Because of the increase in demand for heavy metal detection, electrochemical detection is favorable due to its high sensitivity and efficiency [1].

Currently, stripping voltammetry is the most sensitive method. Stripping voltammetry consider a pre-concentration step in the analysis. Imagine that the electrode first gets dressed and then strips. This method is particularly suitable for heavy metals. In the preconcentration step, the electrode stays in a potential that is cathodic enough to reduce all the metal ions interesting for this analysis [2]. Multiple metals can be co-deposited that way [3].

## Experimental

### Equipment

Applying this method needs a suitable Potentiostat/Galvanostat, such as PalmSens 4, Emstat4S, Emstat3 blue, Emstat4R, etc.



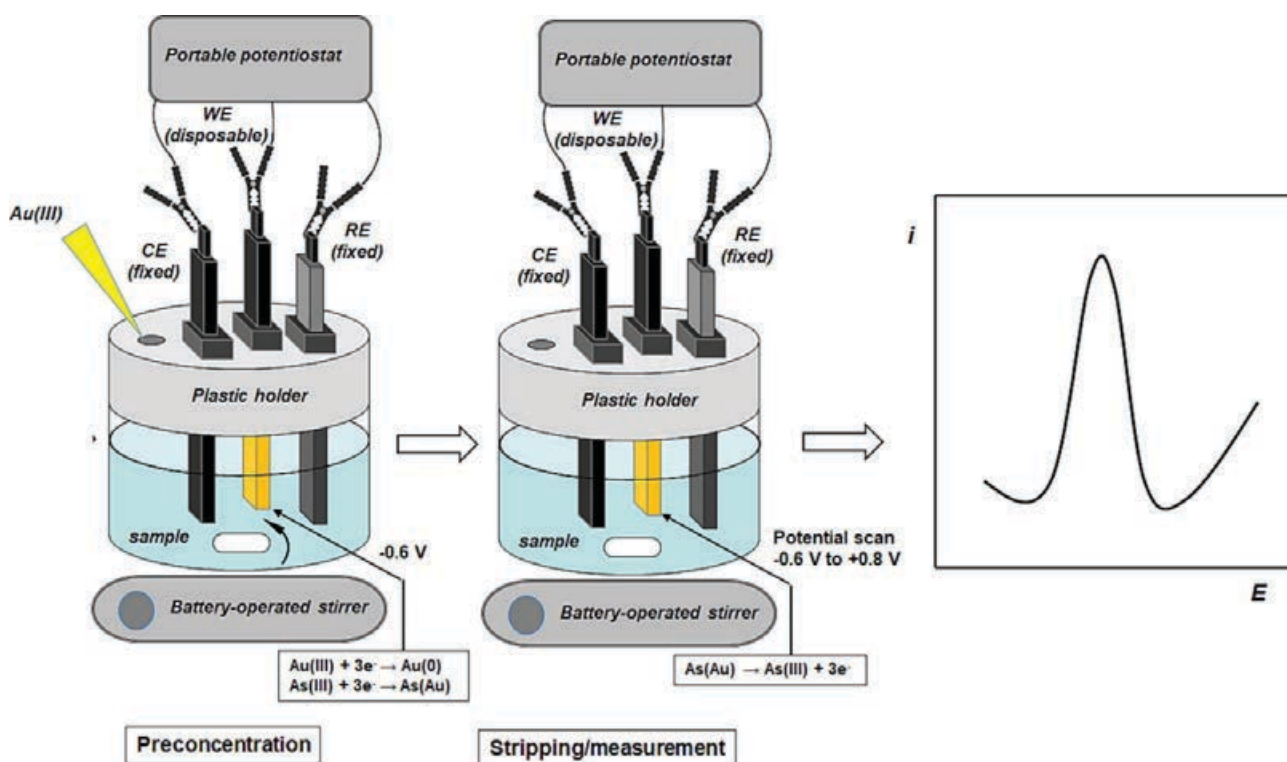
### Chemicals

For each metal make solutions of 5 mg/L of each metal by pipetting of HCl into a bottle. Then add stock metal solution and clean water to a specific volume.

### SPE Electrode Preparation

Since these kinds of electrodes are easily contaminated or destroyed, please do not touch them with bare hands. Cut away the access plastic around one SPE and place it in the connector. The operator must cut the sensor narrow enough for fitting it into the connector, but please take care not to damage the electrodes

or the lines during cutting. The electrode requires conditioning before use, and this is done by running a standard method in HCl. Fill the cell with the HCl, insert the magnetic stirring bar, put the cell on the magnetic stirrer, connect the sensor to the instrument, immerse the sensor in the solution making sure the three electrodes of the sensors are covered with the solution. The exact volume is not important. When finished, rinse the cell and electrode with some HCl solution and clean water. The polymer containing a mercury salt covering the electrode at the beginning of the preparation is now turned into a mercury film.



### Analysis of the Sample

This analysis will be performed using the standard addition method. The standard addition method starts by measuring the sample and then measures the sample again after a known amount of the analyte has been added. If a linear relationship between peak current and heavy metal concentration is given, the concentration of the original sample can be calculated.

### Result and Discussion

The lack of interference and the possibility of knowing the true value allow easy training for this analysis. Interesting samples are river, lakes, oceans, and tap water. To obtain the best results, the user should consider the following points:

1. The pH of the sample should be around 2.5.
2. Fill the cell with the sample and after immersing the connected sensor again, make sure the three

electrodes are covered with the sample solution.

In this method, the technique used is Square Wave voltammetry.

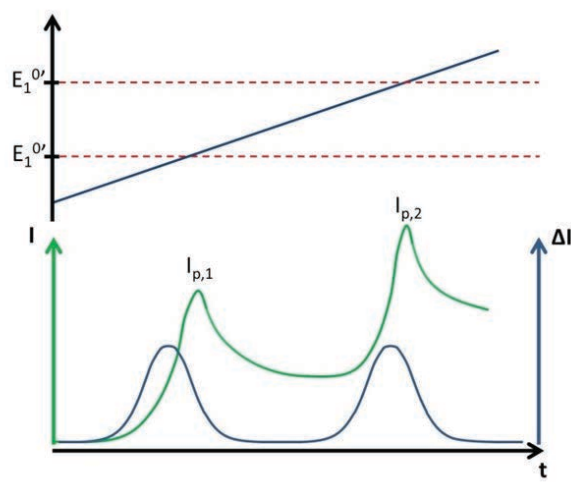


Figure 1: Typical Voltammogram for Analysis of the Sample



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