different Cr values, but reasonably close ($X \approx 0.5$ mg L^{-1} and $Y \approx 0.8$ mg L^{-1}). The results had to be transformed into another form in order to be evaluated. The objective is to measure the difference from the assigned value in a way that allows comparison with defined criteria using the z-score to have unsatisfactory, questionable and satisfactory results. Proficiency testing showed the sequent average results, 77% of laboratories with satisfactory, 16% with unsatisfactory and 7% with questionable results.

The monitoring performance over time was tested using the coefficient of variation (CV %) of the three consecutive rounds. For sample X the CV values of each run were 10.2%, 8.5% and 5.0% and for sample Y, they were 12.6%, 10.1% and 4.4%. These results showed increasing precision performance.

Youden plots, using squaring differences, were used for examining the categories of the unsatisfactory and questionable results. This plot technique provides insight into the nature of corrections that are needed. The results showed that systematic errors were in great number comparing to unexplained errors.

The Proficiency Testing Program by Rede Metrológica RS is a powerful tool for laboratory improvement and quality assurance in testing atomic spectrometry techniques to environmental samples.

Fr37 COMBINED EFFECTS OF INORGANIC ACIDS IN INDUCTIVELY COUPLED PLASMA OPTICAL EMISSION SPECTROMETRY.

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Since inorganic acids are widely used for solid digestion and solution storage, their influence on the analytical signal in ICP OES has been received an increasing interest [1]. In general terms, it has been observed that inorganic acids produce a reduction in the emission intensity with respect to water. The effect has been attributed to various causes, depending on the type of acid and the operating conditions: (i) a change in the sample uptake rate due to a variation in the viscosity, when working under unforced aspiration mode; (ii) a change in the aerosol characteristics due to a variation of the surface tension and volatility; (iii) a change in the solvent and analyte transport efficiency; (iv) a change in the plasma atomization and excitation conditions.

In the sample preparation procedure, wet digestion is the most common method of dissolving solid samples and it often involves the use of a mixture of mineral acids. Aqua regia (HCl:HNO$_3$ (v/v) = 3:1) dissolves most metals including noble metals and it is usually used to perform "pseudototal" attacks on soils and sediments. Perchloric acid is commonly used in conjunction with nitric and sulphuric acids to break up organic materials. For example, a mixture where HNO$_3$:HClO$_4$:H$_2$SO$_4$ (v/v) = 3:1:1 is suitable for a great variety of organic samples.

The combined effect of acids on ICP OES emission intensities might not be the simple addition of the single effects, as already shown for other types of interference [2]. Moreover, the presence of more than one acid probably influences the interference mechanism and the study of

more complicated situations is of great interest to extend knowledge of the ICP OES fundamental processes.

In this work, a multivariate interference study was carried out considering the simultaneous presence of four mineral acids (hydrochloric, nitric, sulphuric and perchloric acid) with their concentrations ranging from 5% to 40% (w/w). A low power inductively coupled plasma atomic emission spectrometer was used, after optimization of operating parameters in order to achieve both plasma robustness and maximum signal to background ratios, favourable for trace element determinations in real samples.

In order to investigate the interference mechanism, the ...eral parameters ...te, aerosol drop ...electron density ...e intensity ratio) ...ences in atomic ...ind subsequent 895-929 (1999). ...ate investigation plasma atomic ic or ultrasonic 89-95 (2000).

Fr38 EVALUATION OF INDUCTIVELY COUPLED PLASMA OPTICAL EMISSION SPECTROMETERS WITH AXIALLY- AND RADIALLY-VIEWED CONFIGURATIONS.

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Inductively coupled plasma optical emission spectrometry (ICP OES) is a well-established technique for multi-element analysis. This technique had a rebirth in the last decade due to the development of equipments with axially viewed configuration and solid state detectors. The idea of axially viewed measurements was proposed in the seventies; however, in spite of the improvement of sensitivity, the system performance was degraded owing to interferences. After two decades, this proposal becomes viable due to the development of proper interfaces based on shear-gas or end-on-gas. However, the common sense in this area recommends ICP OES with axially viewed configuration for applications where sensitivity is critical, but the sample matrix is not complex. In this sense, for samples with complex matrixes it seems that needs a more critical evaluation. In this work, the analytical performance of two ICP optical emission spectrometers with axially- and radially-viewed configurations and charge coupled device solid-state detectors were evaluated using Ar, Ba, Mg and Ni as test elements. The same operational conditions and sample introduction system were employed in both spectrometers

in order to obtain results in similar experimental conditions. The axially viewed configuration used an end-on-gas interface. The figures of merit evaluated were: warm-up time, repeatability, long-term stability, UV and VIS spectral resolutions and limit of detection (LOD) for Ni in 0.14 mol l^{-1} HNO$_3$ and in 1,000 mg l^{-1} Cr media. The robustness, repeatability, long-term stability and UV and VIS spectral resolutions were similar for both configurations. For radially viewed equipment, the warm-up time was lower than that reached using the axially-viewed configuration. On the other hand, the sensitivity attained by the axially viewed configuration was in general 15-fold better than that achieved by using the radially-viewed system. The axially viewed configuration presented higher detection power than that achieved by radially-viewed equipment, even for complex samples. In spite of some particularities, such as the higher warm-up time observed for axially viewed configuration, it could be supposed that the efficiency of the end-on-gas interface improved the performance of this arrangement and it seems that we could suppose that most applications could be perfectly performed at an ICP OES with this arrangement without any serious degradation of analytical performance.

Fr39 THE USE OF DYNAMIC REACTION CELL ICP-MS FOR ENVIRONMENTAL ANALYSES. Kenneth R. Neubauer and Ruth E. Wolf, Perkin Elmer Instruments, 710 Bridgeport Avenue, Shelton, CT 06484-4794

Since its development, ICP-MS has proven beneficial for environmental analyses. This fact has been validated by the approval of government regulated methods, such as US EPA methods 200.8 and 6020 which deal with the analyses of drinking waters, soils, sludges, and waste waters by ICP-MS. Although very beneficial, there are some matrices and analytes where conventional ICP-MS struggles, such as the determination of vanadium, chromium, and aluminum in matrices with large amounts of chloride. Given that environmental matrices may be complex and can contain unexpected amounts of certain species, the ability to eliminate interferences when they occur would be advantageous.

Towards this end, the development of quadrupole ICP-MS instruments with gas-filled cells prior to the quadrupole has shown promise. Given the complex nature of environmental matrices, it is important that the gas-filled cell be able to control the chemistry occurring within, so that new, unexpected interferences do not form in places where interferences are not traditionally observed.

This requirement is fulfilled with Dynamic Reaction Cell (DRC) ICP-MS, which incorporates an active quadrupole for the gas-filled cell. The advantage of this approach is that highly reactive gases may be used to eliminate interferences without worrying about the formation of new interferences. The cell quadrupole functions as a mass filter, only allowing desired masses to pass through to the analyzer quadrupole. Undesired species are ejected from the cell before they can form new interferences, thus providing a controlled reaction environment.

Data will be presented which show how a DRC-ICP-MS is beneficial for environmental analyses in complex matrices. For example, soil digests usually contain high amounts of analytes that normally can be readily determined with conventional ICP-MS using US EPA Method 6020. However, a more thorough digestion approach calls for the use of HCl, which can lead to chloride interferences. Dynamic reaction cell ICP-MS is then beneficial for obtaining the correct results by eliminating interferences. Other specific examples where DRC-ICP-MS may be beneficial will also be shown and discussed.

Fr40 NEW PERSPECTIVES OF PLASMA SPECTROCHEMISTRY. Evgeniy D. Prudnikov and Evgeniy E. Prudnikov, Earth Crust Institute, State University, University emb. 7/9, St. Petersburg, 199034, Russia, evgeniy@EP2256.spb.edu

The development of plasma spectrochemistry methods and instruments, the wide use of the PC computers and the theoretical study of the plasma spectrochemistry methods open the new possibilities for the further improvements of analytical instrument characteristics. The basis of this includes the following:

First of all, the multielement analytical systems are most perspective in this direction. The multielement analysis and the determination of the macro and micro components of analyzed sample give the maximum information about the sample composition, the conditions of the analysis and the different interferences between the sample components. The inductively coupled plasma optical emission spectrometry (ICP OES) and mass spectrometry (ICP-MS) may be most useful in this case, also the other plasma spectrochemistry methods. These methods allow analyzing simultaneously the majority of elements of periodical table with high sensitivity and accuracy.

The second component of this direction is the development of the theory of used analytical methods. The each analytical method has the personal theoretical basis. In second half of twentieth century the topmost development of the atomic emission method theory (the blank and net signal fluctuations, the detection limit calculation) has been obtained by the works of Zaidel, Winefordner, Mandelshtam, Boumans, Prudikov and other scientists). These works open the way for the intensive development of the theory of other spectrometry and analytical methods. The theoretical basis of used analytical method allows extracting the maximum information from the obtained analytical spectrum.

The third component of new analytical systems (NAS) is the use the modern power PC computers. The modern computers allow to work up swiftly the great quantity of the information and to realize the potential possibility of the multielement analytical systems. In this case it is necessary also the improvement of the software for the most effective use of the possibilities of NAS.

And the special importance element of this project is the creation of the universal theory for analytical sciences. The universal theory of analytical sciences gives the possibilities to use the general approach for the different analytical methods and apparatus ant to receive the adequate and comparable results in any analytical systems and information. According to Prudnikov this universal theory of analytical sciences may be realized on the base of the general theory of the standard deviation in analysis, which allows connecting the random errors in analysis with the fundamental characteristics of used method and apparatus (the