Analysis of Aqueous Acid Solutions with Thermo Scientific ARL OPTIM'X WDXRF Sequential Spectrometer

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Key Words
ARL OPTIM'X 200 W, aqueous, acid, liquid, X-ray fluorescence, WDXRF

Goal
A series of water samples with ppm levels of sodium, sulfate and iron are used to compare the performance of ICP analysis with Thermo Scientific™ ARL™ OPTIM'X WDXRF instrument at 200 W.

Introduction
Commonly, aqueous solutions have been analyzed using techniques such as Atomic Absorption (AA) or Inductively Coupled Plasma (ICP). The basic nature of an aqueous solution lends itself nicely in principle to these techniques.

However issues in AA or ICP analysis can arise from dynamic concentration ranges, material falling out of solution, nebulizer plugging or insoluble content. Another issue results from cost of ownership in the case of argon, acid, standards and waste disposal costs.

All of these issues could be resolved by the use of WDXRF in the elemental analysis. WDXRF does have its own issues when compared to AA or ICP because both have lower detection limits and the ability for much better light element analysis (example: Na, Li, B, Be).

Instrument
The ARL OPTIM'X is a WDXRF instrument designed for ease of use with minimal operation and maintenance costs. The instrument is fitted with a Thermo Scientific SmartGonio covering elements from fluorine (^{9}F) to uranium (^{92}U). A rhodium anode X-ray tube is used and the geometry of the instrument is optimized to provide the highest possible sensitivity. Two power versions exist, either 50 W or the new 200 W version which has been used for the tests shown in this report.

The instrument does not require external or internal water cooling, and has 10 times better spectral resolution than a conventional EDXRF instrument as well as superior precision and stability. Good performance is achieved for sodium (^{11}Na), magnesium (^{12}Mg) and even for fluorine (^{9}F). Ease of operation is obtained through the state-of-the-art OXSAS software running under Windows® 10.

Calibration
In an attempt to illustrate the Thermo ARL OPTIM'X, three elements were selected varying in atomic weight and fluorescence absorption rates. The elements selected were sodium (Na), sulfur (as SO_4) and iron (Fe). Elements like Na are highly absorbed by both the liquid cell film and helium purge gas where as Fe is not influenced by either condition.

Calibrations for these elements were created by plotting concentrations of six standard reference materials against analyzed intensities (see illustrations 1 through 3). Unknown samples are then measured to obtain the intensities for each of the elements. The intensities are correlated back to linear regression calibration to calculate the elemental concentrations.

Results
Six unknown samples were provided for analysis. Each sample was analyzed twice by WDXRF and compared to standard ICP results. The duplicate results for heavier elements, such as Fe, will always have smaller standard deviations than lighter elements.

This is due to the liquid cell preparation. The fluorescence escape depth for Fe in a light matrix, such as graphite, is 2720 µm. However, the escape depth for Na in graphite is only 12 µm. When using a thin polypropylene polymer liquid support film at 3.7 µm, Na loses 50% of its fluorescence intensity due to absorption of the film whereas Fe only loses 0.12% of its intensity. Any imperfection in the film will create drastic variation for light element analysis. Table 1 lists the analysis depths for various elements in four different matrices.

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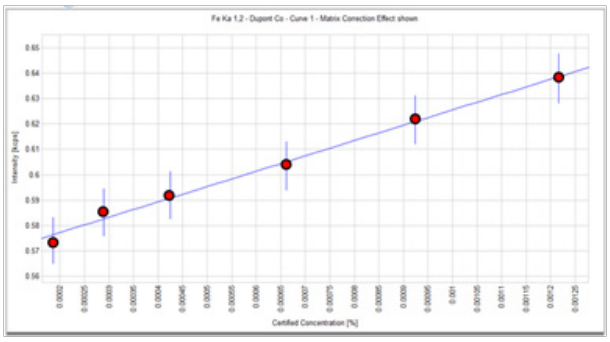

Figure 1: Fe Regression in 60s counting time

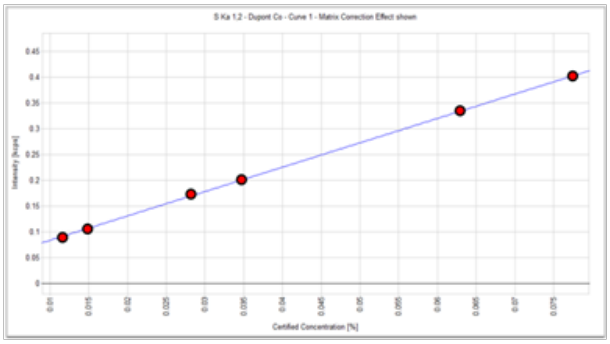

Figure 2: S Regression in 60s counting time

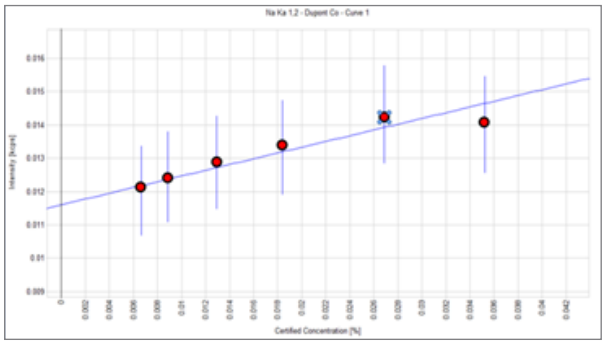

Figure 3: Na Regression in 60s counting time

Table 2 lists each of the ARL OPTIM'X results and the ICP results for each element. Even at these trace elemental concentration levels, the ARL OPTIM'X results provide a high degree of correlation compared to the ICP results and could easily be used as a fast and inexpensive replacement analytical technique to ICP.

Conclusion

The results show that trace elemental liquids analysis can be performed with the ARL OPTIM'X sequential XRF spectrometer. Good precision and accuracy are obtained in this matrix type. Precision can be increased by extending the elemental counting times. This would provide better SD and %RSD at all concentration ranges. Furthermore, operation is made easy through the newest and most advanced state-of-the-art WDXRF OXSAS software which operates with the latest Microsoft Windows® 10 packages.

Analyte	Line	Graphite	Glass	Iron	Lead
Mn	Kα	2110	155	131	9.01
Cr	Kα	1619	122	104	7.23
Ti	Kα	920	73.3	63	4.52
Ca	Kα	495	54.3	36.5	3.41
K	Kα	355	40.2	27.2	3.04
Cl	Kα	172	20.9	14.3	2.19
S	Kα	116	14.8	10.1	4.83
Si	Kα	48.9	16.1	4.69	2.47
Al	Kα	31.8	10.5	3.05	1.7
Mg	Kα	20	7.08	1.92	1.13
Na	Kα	12	5.56	1.15	0.728
F	Kα	3.7	1.71	0.356	0.262
Fe	Kα	2720	196	164	11.1
N	Kα	0.831	1.11	0.0802	0.0713
C	Kα	13.6	0.424	0.0311	0.0312
B	Kα	4.19	0.134	0.01	0.0117

Table 1: Fluorescence Escape Depth (µm)

Sample	Fe (ICP) [ppm]	Fe (XRF) [ppm]	Na (ICP) [ppm]	Na (XRF) [ppm]	SO_4 (ICP) [ppm]	SO_4 (XRF) [ppm]
# 1	3.1	3.9	45	52	86.1	98
# 1 - Dup		3.9		39		102
# 2	1.1	2.0	358	345	78.8	86
# 2 - Dup		1.5		361		83
# 3	7.6	9.1	260	195	411	416
# 3 - Dup		9.5		285		420
# 4	3.0	5.5	180	222	332	337
# 4 - Dup		3.6		206		340
# 5	4.5	4.7	340	303	230	238
# 5 - Dup		5.0		378		246
# 6	4.4	4.9	356	370	87	98
# 6 - Dup		4.5		297		96

Table 2: Unknown sample analysis WDXRF Results vs. ICP Results

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