# EDXRF Application Note

## Trace Elements in Aqueous Solution with UltraCarry®

#1011

### SCOPE

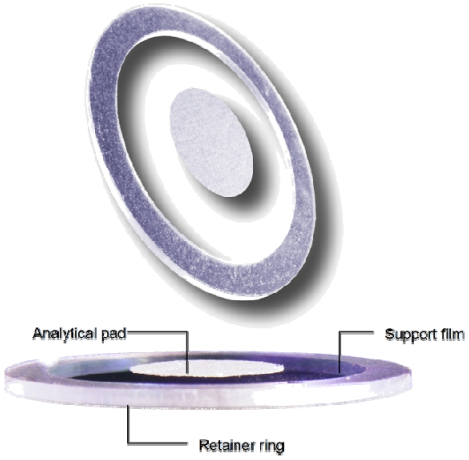
Elemental analysis of aqueous solutions into the low ppm and sub-ppm concentration ranges was demonstrated, using the advanced Cartesian geometry Rigaku NEX CG Energy Dispersive X-ray Fluorescence (EDXRF) spectrometer in conjunction with the patented UltraCarry® sample preparation technique.

### BACKGROUND

Trace element analysis of aqueous-based solutions is important in many areas, such as industrial manufacturing, quality control (QC) and quality assurance (QA) processes, environmental monitoring and remediation, as well as agriculture and general research. To meet the challenges of trace analysis into the ppb range, Rigaku offers the NEX CG EDXRF analyzer and the UltraCarry sample preparation disk. With the Rigaku system, trace analysis can be carried out by non-technical operators and experts alike, without the need for special scientific training and costly, complicated, time consuming sample preparation.


### INSTRUMENTATION

| | |
|---|---|
| **Model:** | Rigaku NEX CG |
| **X-ray tube:** | 50 W Pd-anode |
| **Excitation:** | Indirect with polarization |
| **Detector:** | High performance SDD |
| **Analysis Time:** | 5-20 minutes (depending on application) |
| **Autosampler:** | 15 position w/ 32mm diameter slots |
| **Environnent:** | Vacuum |




### UltraCarry

| | |
|---|---|
| **Type:** | UC-L |
| **Size:** | 32mm diameter |
| **Equipment:** | 0-1000 µL micro-pipette |
| | Rigaku UltraDry® vacuum hotplate |

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## SAMPLE PREPARATION

200 µL of each sample was pipetted onto the center of the UltraCarry pad. Samples were then dried using a vacuum oven (75 torr @ 68ºC for 15 minutes), followed by direct analysis with the Rigaku NEX CG.

# EMPIRICAL APPROACH

## CALIBRATION

To demonstrate the empirical approach, serial dilutions were made from a multi-element ICP certified standard containing the US EPA RCRA elements. Five calibration standards were used to make a calibration for each element over the range 0.1-10 ppm. Typical calibration results are shown here using a 1200 sec analysis time: 600 sec for Cr, Ag, Cd and Ba and 600 sec for As, Se and Pb.

| Element | RMS Deviation (ppm) | $R^2$ |
|---|---|---|
| Cr | 0.027 | 0.99999 |
| As | 0.177 | 0.99954 |
| Se | 0.035 | 0.99998 |
| Ag | 0.187 | 0.99949 |
| Cd | 0.081 | 0.99991 |
| Ba | 0.092 | 0.99988 |
| Pb | 0.075 | 0.99996 |

## RECOVERY and REPEATABILITY

To demonstrate typical measurement recovery and instrument precision, a sample containing 1.00 ppm of each element was measured in 10 repeat analyses using a 1200 sec analysis time: 600 sec for Cr, Ag, Cd and Ba and 600 sec for As, Se and Pb.

| Sample: 1.00 ppm | Units: ppm | | |
|---|---|---|---|
| **Element** | **Average (ppm)** | **Standard Deviation** | **% RSD** |
| Cr | 0.98 | 0.01 | 1.0 |
| As | 1.02 | 0.04 | 3.9 |
| Se | 0.90 | 0.02 | 2.2 |
| Ag | 1.03 | 0.09 | 8.7 |
| Cd | 0.93 | 0.03 | 3.2 |
| Ba | 1.02 | 0.06 | 5.9 |
| Pb | 1.02 | 0.04 | 3.8 |

## TYPICAL DETECTION LIMITS

To determine the Lower Limit of Detection (LLD) with the empirical method, ten repeat analyses of a blank 5% nitric aqueous sample were measured and the standard deviation is calculated. By defining the LLD as three times the standard deviation, this approach ensures that measurements above the determined LLD are measuring signal above background. The following LLDs were determined using the same analysis times employed for calibration. Actual detection limits may vary based on analysis time used, combinations of elements present and aqueous solution composition.

| Element | LLD |
|---|---|
| Cr | 25 ppb |
| As | 65 ppb |
| Se | 40 ppb |
| Ag | 220 ppb |

| Element | LLD |
|---|---|
| Cd | 120 ppb |
| Ba | 100 ppb |
| Pb | 55 ppb |



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## FUNDAMENTAL PARAMETERS APPROACH

A standardless calibration method was built using the Rigaku RPF-SQX fundamental parameters (FP) template for UltraCarry. RPF-SQX is an advanced FP program that automatically deconvolutes spectral peaks and models the thin film sample matrix using first principles. Providing a semi-quantitative measurement of concentrations without the need for known assayed calibration standards, the approach may be used for general screening and monitoring of aqueous solutions, industrial effluents as well as rinse and waste waters. Further refinement of the FP method may be effected by employing a Matching Library using from one to a few assayed samples to model the specific matrix. To demonstrate the standardless FP method, two certified ICP standards, containing common transition metals, were analyzed for 1200 sec.

| Sample Name: Common & Transition Elements<br>Units: ppm | | | | |
|---|---|---|---|---|
| **Element** | **Standard Value** | **RPF-SQX Result** | **Statistical Std Dev** | **Estimated LLD** |
| Mg | 100 | 93 | 2 | 2 |
| K | 100 | 110 | 0.5 | 0.5 |
| V | 10.0 | 11.3 | 0.1 | 0.15 |
| Cr | 10.0 | 11.8 | 0.1 | 0.10 |
| Fe | 10.0 | 11.4 | 0.1 | 0.08 |
| Co | 10.0 | 10.1 | 0.1 | 0.16 |
| Ni | 10.0 | 9.4 | 0.1 | 0.17 |
| Cu | 10.0 | 10.9 | 0.1 | 0.17 |
| Zn | 10.0 | 10.0 | 0.1 | 0.12 |
| As | 10.0 | 8.8 | 0.1 | 0.06 |
| Se | 10.0 | 10.7 | 0.1 | 0.10 |
| Tl | 10.0 | 9.4 | 0.2 | 0.38 |

| Sample Name: Contract Required Detection Limits<br>Units: ppm | | | | |
|---|---|---|---|---|
| **Element** | **Standard Value** | **RPF-SQX Result** | **Statistical Std Dev** | **Estimated LLD** |
| V | 1.00 | 1.24 | 0.03 | 0.04 |
| Cr | 0.20 | 0.29 | 0.02 | 0.04 |
| Mn | 0.30 | 0.51 | 0.02 | 0.03 |
| Co | 1.00 | 1.19 | 0.05 | 0.10 |
| Ni | 0.80 | 1.22 | 0.05 | 0.08 |
| Cu | 0.50 | 0.65 | 0.04 | 0.05 |
| Zn | 0.40 | 0.61 | 0.04 | 0.06 |
| Se | 0.10 | 0.05 | 0.02 | 0.05 |



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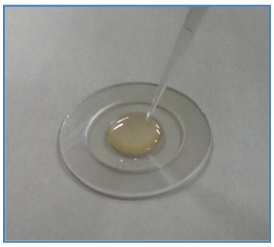
## THE UltraCarry TECHNIQUE

UltraCarry is a novel disposable (single-use) sample carrier used to preconcentrate aqueous samples into a uniform thin film that is optimized for the suppression of background noise. This approach dramatically improves the signal-to-noise ratio of the measurement, resulting in up to two orders of magnitude improvement in the LLD (Lower Detection Limit), for both heavy and light elements, relative to conventional bulk liquid sample presentation.

The design is comprised of a ring-shaped support fitted with an X-ray transmissive film and patented central analytical pad. This design allows the liquid sample to dry in an even single layer, eliminating or minimizing the formation of concentric rings of dry sample material, giving a more consistent and repeatable XRF measurement. Using the automatic sample changer, up to 15 samples can measured in a single batch without operator intervention. The UltraCarry technique is amazingly simple, requiring only three easy steps, making it an ideal tool for non-technical operators to routinely perform trace element analysis without a wet lab.

1. Spot UltraCarry



2. Dry the samples

3. Analyze

## CONCLUSION

The Rigaku NEX CG combines secondary and polarization target excitation, with a high performance SDD detector, to deliver optimal EDXRF sensitivity. In conjunction with UltraCarry, the NEX CG is an ideal tool for the trace elemental analysis of aqueous solutions down to parts-per-billion levels. This technique is suitable for many applications, including:

### Industrial

- Monitor effluents. waste streams and discharge waters
- Screen for common metals
- Measure hazardous elements
- QC of production rinse waters

### Environmental

- Pavement run-off
- Storm water run-off
- Agricultural run-off
- Site remediation
- Soil leachates



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