

Automated Liquid-Liquid Extraction of Copper using ACORGA® Reagent on a VERSA Mini LLE Workstation

Sikander Gill PhD, Rajwant Gill PhD, Marco Garate PhD and Dong Liang PhD
Aurora Biomed Inc, Vancouver, BC, Canada



I. Abstract

Liquid-liquid extraction, also known as solvent extraction and partitioning chromatography, is employed to separate compounds based on their relative solubility's in two different immiscible liquids. This is a basic technique in chemical laboratories, where it is performed using a separatory funnel, which is a cumbersome procedure when processing a large number of samples. Aurora Biomed's automated VERSA workstation provides a simple and effective solution for analytical- and preparative- scale separation of diverse molecules like vitamin D, beta-carotene, and other biomolecules.

Recent advances in design and development of extractants capable of metal ion recognition or of strong complex formation in highly acidic media, have significantly improved the utility of the technique. Some of these solvents were used to validate the extraction of copper ions on the VERSA Liquid-Liquid Extraction Workstation. The protocol steps included dilutions, solution preparation, liquid-liquid extraction isotherms, and production of an s-curve for the process.

II. Introduction

Liquid extraction for copper was first used commercially in 1968 and the copper specific ligands were based on formulations of ketoxime. These were followed by next generation ketoxime based formulations¹. Among such formulations, the ACORGA® line of products for copper solvent extraction presented great advantages for mining companies in extraction processes. The ACORGA® reagent has been reported to perform with the following merits²⁻³.

- Excellent extraction and stripping kinetics
- High extraction efficiency over a wide pH range
- High recovery of Cu from concentrated sources

In order to automate the ACORGA® extraction process to carry solution preparation, liquid-liquid extraction isotherms, and s-curve production, Aurora Biomed Inc validated this process on a VERSA LLE Workstation.

III. Objectives

- To validate the VERSA LLE workstation for Copper extraction
- To optimize the automated protocol
- To compare automated versus manual performance
- To study the reproducibility of auto performance

IV. Materials & Methods

The validation of the automated process of liquid-liquid extraction on a Versa Workstation was conducted as follows:

- 1. Aqueous phase sample preparation:** The samples were prepared by spiking water samples with copper sulphate (8 g/L) adjusted with dilute sulphuric acid to pH 2.0.
- 2. Organic phase extraction solvent preparation:** 10% (volume) of ACORGA® (Cytec Industries Inc, Woodland Park, New Jersey, USA) in extraction grade kerosene.
- 3. Automation protocol:** The automated protocol for liquid-liquid extraction is depicted in Figure 1.
- 4. Deck equipment (Figure 2):**
 - a. Sample rack:** The samples added to glass tubes [12 mm (diameter) x 75 mm] were placed in a rack on deck position 2.
 - b. Extraction rack:** The extraction was carried in glass tubes [12 mm (diameter) x 75 mm] inserted in a rack (6 x 8 format) which was equipped on a heater shaker on the deck.
 - c. Organic phase extraction solvent preparation:** The solvent was dispensed through one of the ReagentDrop channels from a bottle (500 mL) placed outside the deck of the VERSA 110 LLE Workstation.
 - d. Tip boxes:** The tip boxes (200 and 1000 µL) were placed on the deck in positions 1 and 4.
- 5. Kinetics and isotherms optimization:** The kinetics and isotherms were performed as described in results and discussion section.
- 6. Manual performance:** The process was also carried manually using standard manual-pipettor.
- 7. Analysis:** After the extractions, the extracted samples were analyzed on a TRACE AI1200 atomic absorption spectrometer (Aurora Biomed Inc, Vancouver, BC, Canada) for copper concentration in both the aqueous and organic phases. The analysis was performed using the following formula: (% extraction = $100 \times [\text{Cu}]_{\text{org}} / ([\text{Cu}]_{\text{org}} + [\text{Cu}]_{\text{aq}})$), where org: organic phase, aq: aqueous phase.

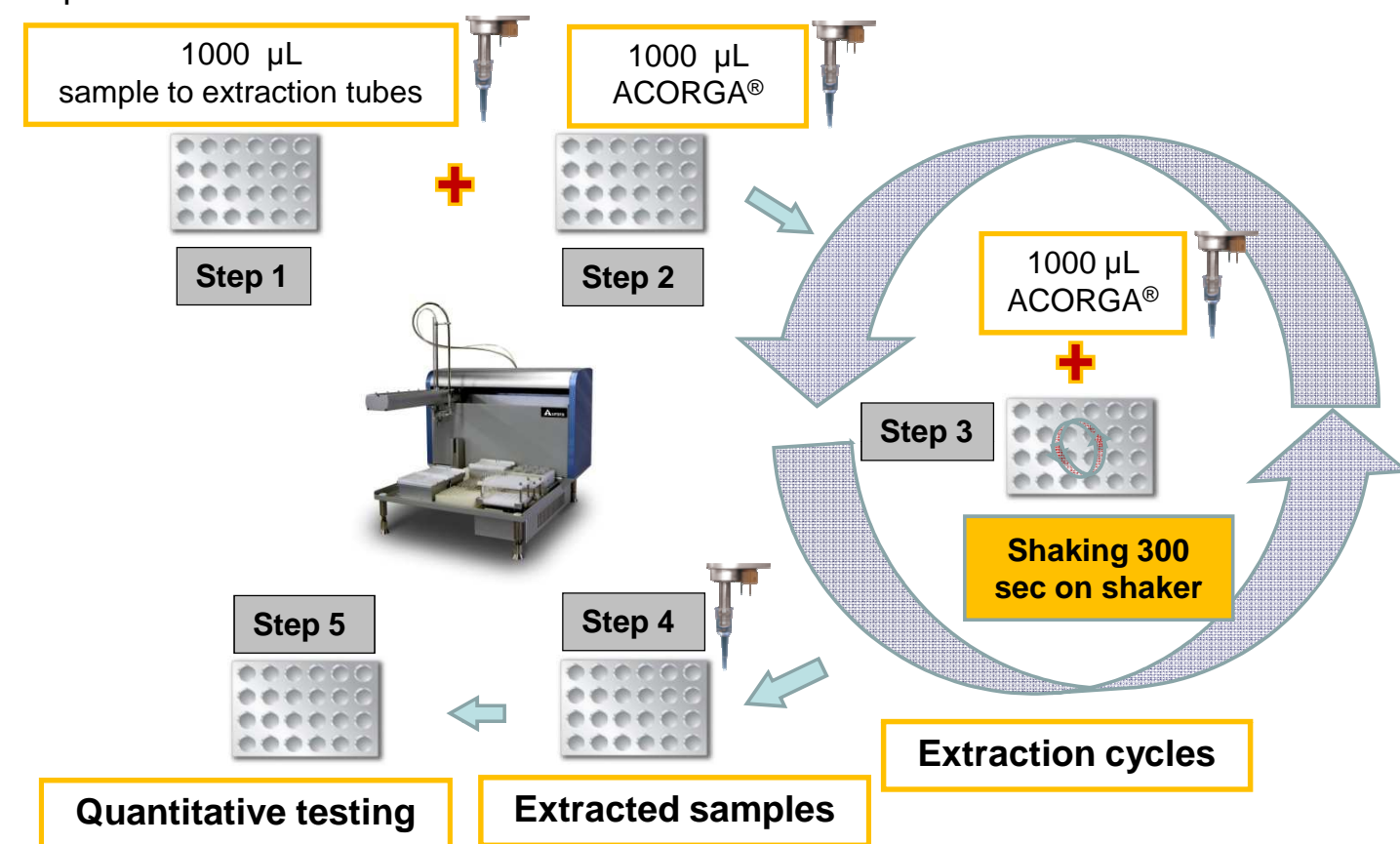


Figure 1: Automation of typical protocol for copper liquid-liquid extraction on VERSA 110 LLE Workstation.



Figure 2: Deck layout of the VERSA Workstation for Copper stripping and extraction.

V. Results & Discussion

The automated process of extraction of copper on VERSA Workstation using ACORGA® reagent was very effective when used in stripping and extraction of copper from copper mines.

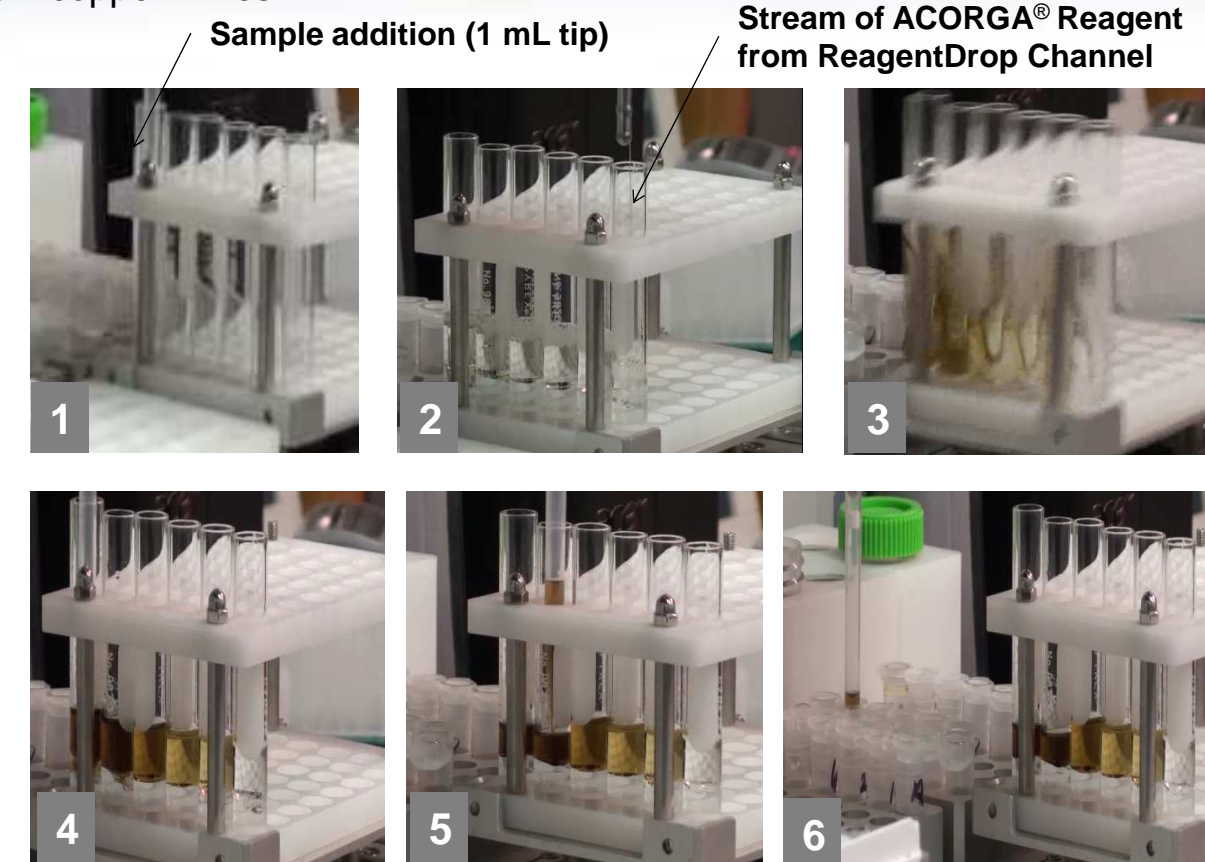


Figure 3: Steps of the copper extraction process using ACORGA® reagent and VERSA LLE workstation

The steps 1 to 6 (Figure 3) represent: The addition of sample (1.0 mL) using a single channel SyringePipettor (step # 1), addition of ACORGA® reagent (1.0 mL) using a single ReagentDrop channel (step # 2), vigorous orbital mixing of solution (step # 3), rendered brown organic and colorless aqueous phases (step # 4), organic phase removal using 1 mL tip (step # 5), and transferring of extracted organic phase into the target vials (step # 6). The brown color gradient is the result of extraction from samples containing 1 mL of 6.0, 3.0, 1.5, 0.75, 0.35, and 0 g/L CuSO₄, respectively.

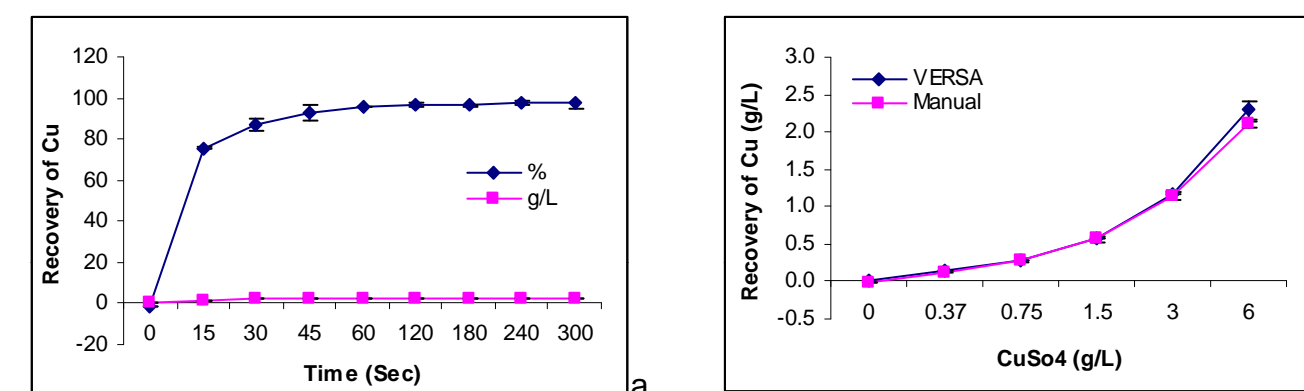


Figure 4: Extraction of copper using ACORGA® reagent: (a) Optimization of extraction time. (b) Comparison of manual and automated process.

The extraction process was optimized for extraction time from 15 sec to 300 sec on thermal shaker and at room temperature (Figure 4a). The data showed that the recovery (%) of copper was maximized at 300 seconds of extraction. In order to compare the automated and manual extraction methods, the extraction process was carried out for samples containing 6.0, 3.0, 1.5, 0.75, 0.35, and 0 g/L CuSO₄. The data (Figure 4b) indicated that the extraction efficiency was similar for both the manual and automated processes. However, the efficiency of extraction decreased from lower to higher concentrations of Cu in the extraction vessels (data not shown).

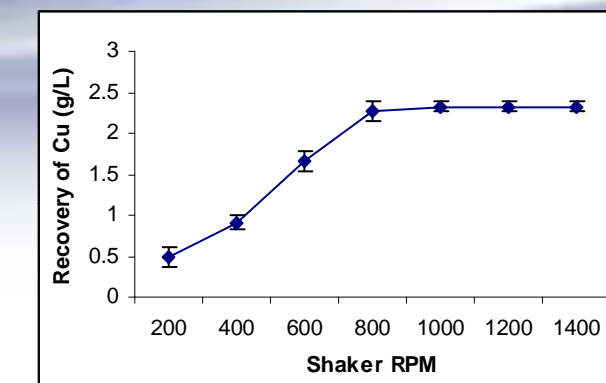


Figure 5: Optimization of shaking speed on the thermal shaker:

Three extraction tubes containing 6g of CuSO₄ solution were arranged in the A1, C1, and F1 slots of the rack placed on the thermal shaker equipped on the deck of the system. The extraction was carried at several speeds the shaker. It was observed that the extraction efficiency was a function of the shaking speed (rpm) ranging from 200 to 1000 rpm, while no significant difference was found in extraction efficiency from 1000 to 1400 rpm suggesting that a shaking speed of 1000 rpm on the thermal shaker was optimal for the extraction process (Figure 5).

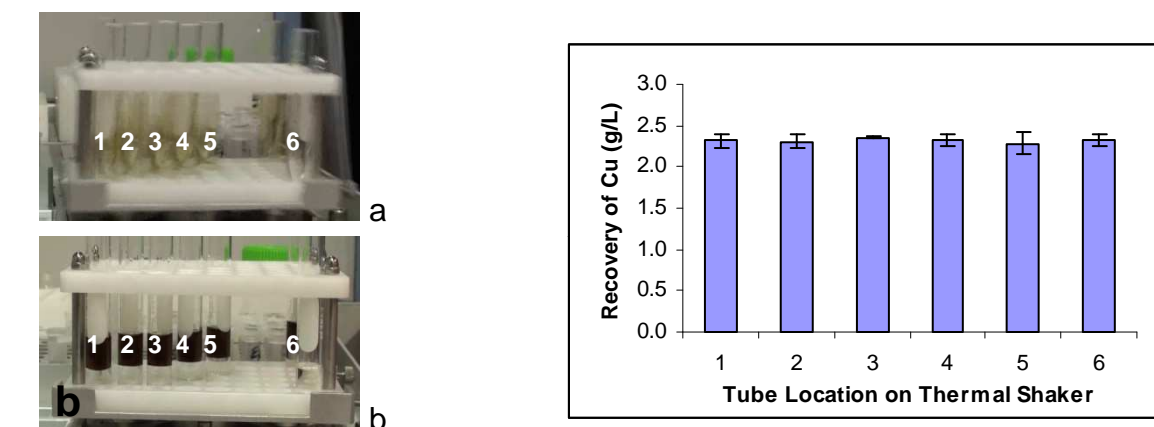


Figure 6: (a-b) Distribution of tubes to determine the uniformity of shaking effect from the centre of the rack placed on thermal shaker to its periphery. (c) Extraction data obtained in this assay.

The distribution of the extraction tubes containing 6 g of CuSO₄ solution shaken at 1000 rpm on the thermal shaker at room temperature resulted in a non-significant difference in extraction efficiency between the tubes at the centre and the periphery of the rack placed on the shaker (Figure 6a-b). The extraction data did not show a significant difference in extraction efficiency among the 6 tubes when taking rack position into consideration (Figure 6c).

VI. Conclusion

Liquid-liquid extraction of copper using ACORGA® reagent for copper stripping and extraction can be effectively performed by a VERSA workstation achieving optimal results for various kinetic studies.

VII. Acknowledgements:

The authors acknowledge Saranna Brugger for her skilful editing of this poster.

VIII. References

1. Akash *et al.*, Recovery of copper from zinc leaching liquor using ACORGA M5640. Separation and Purification Technology, 2010, 76 (1):21-25.
2. Virning *et al.*, Effects of nitrate on copper SX circuits: A case study, Copper 2003 – Cobre 2003, Volume VI – Hydrometallurgy of Copper (Book 2). The Canadian Institute of Mining, Metallurgy and Petroleum, Montreal, Quebec, Canada, 795-810.
3. Swart *et al.*, Evolution of copper solvent extraction reagents, Hydrocopper 2007, IV International Cooper Hydrometallurgy Workshop, Viña del Mar, Chile, 41-47. www.cytect.com/specialty-chemicals/solvent-extraction.htm