Simultaneous Determination of Stainless Steel Components in Urine Samples using ICP-DRC-MS

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Introduction and Background

We report an analytical method for the simultaneous determination of chromium (Cr), iron (Fe), nickel (Ni), and vanadium (V) in urine samples obtained from steel workers using an ICP-MS equipped with Dynamic Reaction Cell (DRC) technology. Improvements in methodology produce low-level detection limits, reduced analysis times, and increased instrument stability.

Steel is "stainless" if it is comprised of more than 11.5% Cr. Stainless steel often contains Ni and V. Cr offers corrosion resistance, while Ni improves low temperature malleability. V is often added to steel for specialty purposes, such as to create steel for use in surgical instruments.

In the high temperature settings of a working steel mill, some Fe, Ni, Cr, and V will become volatile or atmospherically suspended and subject to inhalation. Ni and V dusts are known respiratory irritants, while Cr and Ni compounds are suspected carcinogens. Exposure to atmospheric Ni and V2O5 are regulated by OSHA, and the effects of inhalation of certain species of Cr have been well studied. The presence of metals in the urine of industrial workers can indicate occupational exposure; however, low background concentrations of these metals in urine can hinder accurate quantification for treatment or exposure studies.

The Analytical Challenge

The matrix components of urine include salts, urea, and other organic molecules, such that urine may be up to 5% solids by volume. High solids levels and salt-based polyatomic interferences form a significant obstacle to low-level ICP-MS analysis. To prevent disruptions in the sample introduction system, urine samples typically are diluted 1:9 in low concentration acid solutions prior to analysis. Analyzing the samples at greater dilutions can address some of the analytical difficulties; however, this may lead to decreased precision and increased detection limits. Even at moderate dilutions such as 1:9, a gradual build-up of solids will occur in the sample introduction system and on the ICP interface cones, affecting instrument sensitivity. High levels of ions entering the lens region will cause ion dispersion, lowering internal standard recoveries, and possibly leading to bias in the analysis.

Approach

Reduce instrument exposure to high-matrix urine samples by reducing the per-sample analysis time:

- Develop DRC optimization settings that allow for a constant DRC gas flow while still overcoming polyatomic interferences for all metals of interest.
- Use SC-FAST to reduce time required for sample to reach the instrument and reduce exposure to matrix when not quantifying analytes.

Prior to analysis, samples are diluted with acidic solution and digested with heat to dissolve suspended solids and allow for more complete analysis.

Experimental Instrumentation Setups

Table 1

Setup No.	Sample Introduction	Nebulizer Type	Flow Rate (mL/min)
1	Cetac-520HS	Quartz Meinhard	1.2
2	Cetac-520HS	PFA-ST	1.2
3	ESI SC-FAST	PFA-ST	0.3

Two sets of 50 samples were analyzed with a Cetac-520HS autosampler as specified in CDC biomonitoring methodology for trace metals in urine, and a Meinhard quartz nebulizer with sample uptake at 1.2 mL/min. 100 samples were analyzed with a Cetac-520HS autosampler and a PFA-ST nebulizer with sample uptake at 1.2 mL/min. One set of 150 samples was analyzed with an ESI SC-Fast sample introduction system and a PFA-ST nebulizer with sample uptake at 0.3 mL/min.

Methods and Materials

In response to the above challenges, a method utilizing specialty techniques and advanced instrumentation was developed in hopes of producing lower detection limits and higher stability than commonly reported by ICP-MS (Table 1).

Analytical Parameters

Table 2

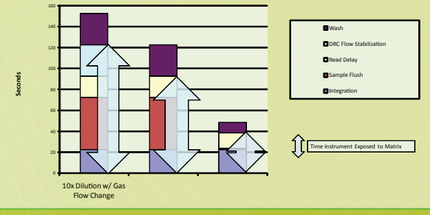
Instrument:		Elan DRC-II
Spray Chamber:		ESI PC3
Spray Chamber Temperature:		2 °C
RF Power:		1400 W
Nebulizer Gas Flow:		~ 1 L/min
Auxiliary Gas Flow		1.2
Plasma Gas Flow		15
DRC Settings:		NH_3 Flow/RPq
	Cr	0.8/0.50
	Fe	0.8/0.70
	Ni	0.8/0.25
	V	0.8/0.80
Internal Standards:	Cr	Y
	Fe	Sc
	Ni	Sc
	V	Ga
Dilution:		10x
Diluent:		1% HNO_3
Rinse Solution:		2% HNO_3

Sample Collection and Processing: 300 raw urine samples were obtained from the Harvard School of Public Health after collection from steelworkers who were occupationally exposed to the target analytes. After collection, samples were frozen and remained frozen for 4 years (Figure 1). Samples were thawed prior to analysis in a Class 100 laminar flow clean hood. An aliquot was taken and diluted 1:9 in 1% (v/v) HNO_3. Matrix spikes were added with the diluent. In order to dissolve the suspended solids, the samples were capped and heated to 90° for at least 30 minutes, longer if suspended matter remained visible. After heating the vials were allowed to cool and sampled directly by the instrument autosampler.

Results and Discussion

Per-Sample Analysis Time by Method

Figure 2



Analytical method Set-up No. 1 requires that the instrument be exposed to the aspirated sample for over 120 seconds per sample. Set-up No. 2 represents the development of a DRC flow regime that was able to overcome polyatomic interferences at a constant cell gas flow eliminated the need to include a flow stabilization period in each run, reducing instrument-sample exposure by 30 seconds each run. Set-up No. 3 replaced a peristaltic pump sample delivery system with a pneumatically driven one (SC-FAST) and greatly decreased the per-sample run time, from 123 seconds to 49 seconds. More importantly, Set-up No. 3 decreased the time during which the instrument was exposed to the aspirated sample, without integrating, from 70 seconds per run to 16 seconds (Figure 2).

A PFA–ST micro-flow nebulizer allowed a 75% reduction in rate of sample aspiration, from 1.2 mL /min to 0.3 mL/min, without any loss of sensitivity, contributing to a reduction in salt buildup, compared to analysis with a quartz Meinhard nebulizer.

Standard Reference Material Results

Table 3

		NIST 2670a - Low Level				NIST 2670a - High Level			
	Setup No.	Cr	Fe	Ni	V	Cr	Fe	Ni	V
Reference Value		2	N/A	2	< 1	20	N/A	100	30
Achieved Results	1	0.67	18	1.4	0.42	22	17	90	24
	2	1.3	14	1.8	0.39	26	12	93	24
	3	1.3	18	1.7	0.41	25	20	90	24

SRM recovery for the various sample introduction systems: For the high level SRM, NIST 2670a, freeze dried urine, there did not appear to be any significant difference in recovery; however, for the low level SRM, the use of a PFA ST nebulizer gave significantly higher values for Cr recovery, and slightly higher recovery for Ni (Table 3).

NIST 2670a lists informational concentration values for Cr, Ni, and V. Results obtained for these analytes were consistent across multiple isotopes (when applicable) and analytical days, and were close to the published informational values. Changes in the sample introduction system did not significantly change the SRM recoveries, though internal standard recoveries during the analysis of the SRMs did improve.

Method precision was assessed by repeated matrix spikes on urine at 2-5x the MDL; method accuracy was assessed by repeated analysis of NIST SRM 2670a.

Sample Introduction	Element	Mean Spike Recovery (%)	Mean RPD (%)
Cetac-520HS	Cr	84.7	9.7
	Fe	85.8	7.6
	Ni	80.9	3.5
	V	103.3	9.9
ESI SC-FAST	Cr	98.5	2.4
	Fe	98.3	3.6
	Ni	85.7	3.4
	V	93.8	3.4

Table 4

Table 4 displays average matrix spike recoveries for two analytical runs using a peristaltic pump sample delivery system and one analytical run using a pneumatic sample delivery system. For three of the four elements, matrix spike recovery improves significantly, and for the remaining element, V, the average matrix spike recovery decreased from 104 to 94%. The average RPD of spikes decreases for all elements.

Matrix Spike (Cr) Recoveries

Figure 3

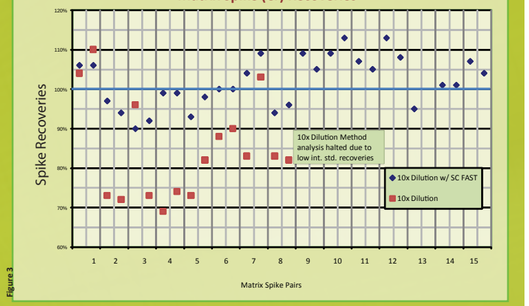


Figure 3 shows calibration verification-corrected Cr matrix spike recoveries for three analytical runs. The first two used a peristaltic pump delivery system and are displayed as 10x dilution. The average matrix spike recovery for the two runs was 84.7%, with a standard deviation of 12.8%. Also displayed are Cr matrix spike recoveries for a single analytical run using the pneumatically driven sample delivery system. Here the average spike recovery is 98.6% and the standard deviation is 5.5%.

A 10x dilution with an acid solution is the primary preparation method for the analysis of metals in urine samples in the literature. Figure 3 and Figure 5 show that this method, when performed with a ICP-MS with DRC technology, a Cetac-520HS autosampler, and a Meinhard nebulizer, lead to decreasing sensitivity and low matrix spike recoveries. Internal standard recoveries for this analysis were consistently low (between 40-60%). Using PFA-ST nebulizer and an SC-FAST sample introduction system, Ga internal standard recoveries improved to 80-100% for the first 150 runs, then exhibited a gradual, steady decline. As Figure 3 shows, Cr matrix spikes showed dramatically improved recoveries when changing sample introduction systems, initially recovering at 70-90%, and improving to 90-110% with the SC-FAST sample introduction system. Duplicate RPDs also decreased dramatically, with the average Cr spike RPD in the 2.4-3.6% range with the SC-FAST, compared to 3.5-9.9% with the original sample introduction system.

Method Detection Limits

Table 5

Element	Isotope	Reported MDL (µg/L)	Achieved MDL (µg/L)	Samples Quantified Above MDL
Cr	52	0.043	0.043	85%
Fe	56	4.8	4.8	100%
Ni	60	0.35	0.35	95%
V	51	0.032	0.032	84%

Method Detection Limits: MDLs for this analysis were determined by repeatedly spiking composite urine collected from volunteers in our trace metals laboratory. Four replicates of the bulk urine were analyzed to determine blank levels, and then 8 replicates were spiked and analyzed to calculate the MDL and observed spike recovery. The MDL was determined by multiplying the student-t value for n-1, 2.998, by the standard deviation of the spiked sample results. The determined MDLs are listed in Table 5.

Figure 4a

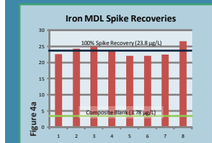


Figure 4b

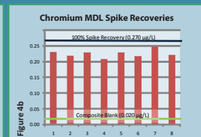


Figure 4c

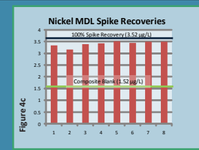
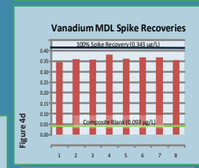


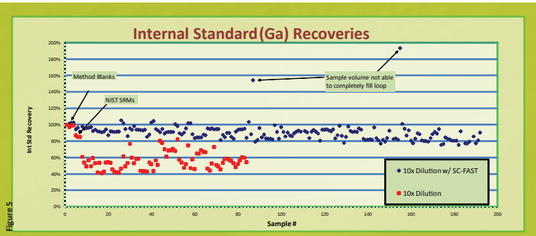
Figure 4d



This poster presents some of the lowest MDLs for Cr and V in urine reported, and possibly the lowest obtained by repeated spiking of urine.

Internal Standard(Ga) Recoveries

Figure 5



Internal Standard Recoveries: The above graph displays Ga recoveries on two analytical runs. The 10x dilution run used a peristaltic pump to deliver sample to the nebulizer, at a rate of 1.2mL/min. The immediate drop in internal standard recovery can be seen when the NIST SRMs are analyzed, followed by a further drop when the analysis of samples occurs. The 10x Dilution w/ SC FAST run used a sample loop and back pressure peristaltic pump to deliver sample at a rate of 0.3mL/min. The internal standard recoveries still drop over the course of the run; however, the decrease is gradual and steady, never falling below 70% recovery in the first 190 runs.

Conclusion

This method produced significantly improved internal standard recoveries for samples and maintained higher internal standard and matrix spike recoveries for samples and QA standards over extended runs than the CDC method for trace metals analysis in urine by ICP-MS.

The detailed advancements used in analytical method Set-up No. 3 (using an ESI SC-FAST autosampler, PFA-ST low-flow nebulizer, and ICP-MS with DRC technology) enable the quantification of metals in samples at previously undetectable levels. The expense and time needed for the analysis are drastically reduced, allowing for more complete sampling. A more complete and useful dataset is given from the universal detection of these analytes.

References

1. CDC Toxicity Reports for Chromium (U.S. Department of Health and Human Services, Public Health Service Agency for Toxic Substances and Disease Registry, September 2000); Vanadium (U.S. Department of Health and Human Services, Public Health Service Agency for Toxic Substances and Disease Registry, August 2005); Nickel (U.S. Department of Health and Human Services, Public Health Service Agency for Toxic Substances and Disease Registry, July 1992).
2. Harvard Reference
3. CDC Draft SOP ITU0018. Urine Multi-Element ICP-DRC-MS, October 21, 2005.

Acknowledgements

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The Institutional Review Board at the Harvard School of Public Health approved the study protocol, an d informed written consent was obtained from each adult prior to participation.

Baseline blank urine, used for MDL studies, was donated by the Trace Metals Research Group at Brooks Rand Labs.