APPLICATION NOTE

ICP-Optical Emission Spectroscopy

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Determination of Various Elements in Semiconductor-Grade Phosphoric Acid by ICP-OES

Introduction

In the manufacture of semiconductor products, the purity of the reagents is of utmost importance since the presence of contaminants can affect the performance of the final products. Phosphoric acid is commonly used in the production of various semiconductor materials and, therefore, requires trace levels to be measured as specified in the SEMI C36-1107 Grade 3 requirements. Phosphoric acid presents an analytical challenge due to its viscosity, composition, and concentration. The combination of matrix composition and measurement levels make phosphoric acid an ideal candidate for analysis by ICP-OES. This work describes the analysis of phosphoric acid with ICP-OES to meet the SEMI requirements.

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Experimental

All analyses were carried out on a PerkinElmer Optima® 8300 ICP-OES which uses flat induction plates (Flat Plate™ plasma technology) instead of the traditional helical load coil. This innovative technology delivers a plasma generation system that does not require coil cooling and is capable of operating at a plasma argon flow as low as 8 L/min. The operating conditions are listed in Table 1.

To avoid contamination from the lab environment, samples were prepared in a clean hood, and the autosampler was covered. All sample preparation was done in PFA bottles which were pre-soaked in 5% (v/v) nitric acid for 24 hours, then filled with ultra-pure water for storage before use. In order to eliminate contamination from the pump tubing, self-aspiration was used.

All measurements were made against calibration curves using the Method of Additions Calibrations, with 5 ppb, 10 ppb and 20 ppb standards. For analysis, ultra-pure grade phosphoric acid (H_3PO_4) was diluted ten times with deionized water.

Table 1. Sample introduction system and plasma parameters

Parameter	Condition
Injector:	Alumina 2 mm i.d.
Spray chamber:	Cyclonic
Nebulizer:	Meinhard
Sample tubing:	Capillary
Drain tubing:	1.14 mm i.d.
Quartz torch:	Single slot
Sample capillary:	PTFE 1 mm i.d.
Sample vials:	Polypropylene
Equilibrium delay:	15 sec
Plasma aerosol type:	Wet
RF power:	1300 W
Nebulizer flow:	0.55 L/min
Auxiliary flow:	0.2 L/min
Plasma flow:	8 L/min
Sample uptake:	Self aspiration
Plasma viewing:	Axial
Processing mode:	Peak area
Auto integration:	5 - 10 sec
Replicates:	3
Background correction:	1 or 2-point

Results and Discussion

Table 2 shows the elements, wavelengths, correlation coefficients, and detection limits of the method. The detection limits, determined from 25 replicate measurements of the sample, are within the SEMI 36-1107 criteria. The low detection limits are an indication of the system's short-term stability. The elevated Pb detection limit results from the higher level of Pb in the acid.

Table 2. Elements, wavelengths, correlation coefficients, and detection limits

Analytes and Wavelengths (nm)	Correllation Coefficients	Detection Limits (ppb)
Al 396.153	0.997	1.86
Ba 233.527	0.999	0.529
Be 313.107	0.999	0.119
Ca 317.933	0.999	0.640
Cd 228.802	0.996	0.909
Co 228.616	0.998	0.794
Cr 205.560	0.999	0.838
Cu 327.393	0.999	0.953
Fe 239.562	0.999	0.736
K 766.490	1.000	8.71
Li 670.784	0.997	0.205
Mg 285.213	0.998	0.253
Mn 257.610	0.999	0.176
Mo 202.031	0.999	1.86
Na 589.592	0.999	0.523
Ni 221.648	0.999	1.22
Pb 220.353	1.000	8.56
Sn 189.927	0.999	3.83
Ti 334.940	0.999	0.172
V 290.880	0.999	0.690
Zn 202.548	0.999	0.527

To ascertain the accuracy and robustness of the method, a spike recovery test was carried out. The H_3PO_4 was divided into three containers, and each analyzed. A 5 µg/L spike was then added to each container and re-analyzed. The spike recoveries, shown in Table 3 (Page 3), ranged from 90-111%, well within the SEMI requirement of 75%-125%.

Table 3. Repeatability and recovery of 5 µg/L spikes

Analyte and Wavelength	Sample 1	Sample 2	Sample 3	Sample Avg	Spike 1	Spike 2	Spike 3	Spike Avg	Recovery
Al 396.153	0.161	0.586	-0.039	0.236	5.58	5.07	6.09	5.59	107%
Ba 233.527	1.01	0.660	0.869	0.848	5.74	5.82	5.88	5.81	99.3%
Be 313.107	0.076	0.071	0.067	0.071	5.00	4.99	4.99	4.99	98.4%
Ca 317.933	0.604	0.776	0.719	0.700	5.58	5.21	5.80	5.53	96.6%
Cd 228.802	11.7	11.6	11.8	11.7	16.6	16.6	16.8	16.7	99.6%
Co 228.616	6.11	6.06	6.11	6.09	11.1	11.1	11.2	11.1	101%
Cr 205.560	5.41	5.38	5.47	5.42	10.9	10.4	10.4	10.6	103%
Cu 327.393	3.08	2.87	2.56	2.84	7.77	7.76	7.69	7.74	98.1%
Fe 239.562	1.36	1.62	1.71	1.56	6.17	6.60	6.57	6.45	97.7%
K 766.490	-9.72	-9.50	-9.24	-9.49	-4.14	-3.67	-3.98	-3.93	111%
Li 670.784	1.31	1.25	1.16	1.24	6.15	6.10	6.11	6.12	97.6%
Mg 285.213	-0.071	0.069	-0.013	-0.005	5.06	5.11	5.14	5.10	102%
Mn 257.610	0.581	0.591	0.602	0.591	5.53	5.49	5.51	5.51	98.4%
Mo 202.031	-1.39	-1.68	-1.56	-1.54	4.11	3.61	4.03	3.92	109%
Na 589.592	0.424	0.590	0.498	0.504	5.49	5.46	5.44	5.46	99.2%
Ni 221.648	-1.41	-1.06	-1.11	-1.19	3.71	3.63	3.86	3.74	98.5%
Pb 220.353	21.0	21.3	23.1	21.8	26.2	25.9	26.8	26.3	89.5%
Sn 189.927	-0.667	0.175	-0.088	-0.193	4.66	4.20	4.49	4.45	92.9%
Ti 334.940	0.276	0.354	0.292	0.307	5.26	5.28	5.30	5.28	99.4%
V 292.402	0.218	0.008	0.124	0.117	5.08	5.18	5.04	5.10	99.6%
Zn 202.548	-0.695	-0.806	-0.605	-0.702	4.33	4.129	4.20	4.22	98.4%

To verify the stability of the method, a 5 µg/L spike solution was aspirated continuously for an hour, with measurements being made consecutively. Figure 1 shows the resulting stability plot, where results were normalized to the average reading. The variations were generally less than ± 10%, indicating no significant drift. This result demonstrates the robustness of the Optima 8300's Flat Plate plasma to handle a complex matrix at a low plasma gas flow.

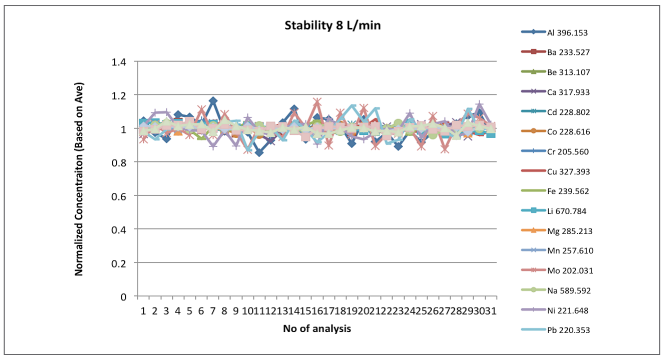

Figure 1. Stability plot for continuous aspiration of a 5 µg/L spike in H_3PO_4 measured over one hour.

Conclusion

This work has demonstrated that the Optima 8300 ICP-OES can effectively analyze phosphoric acid to meet the specifications of SEMI 36-1107. Utilizing Flat Plate plasma technology, only 8 L/min of argon gas are needed, significantly reducing operating costs. Even with low argon consumption, a robust plasma is produced, which results in signal stability in complex matrices and low detection limits. The combination of low argon consumption and robustness makes PerkinElmer's Optima 8300 ICP-OES ideally suited for the analysis of complex samples, while minimizing operating costs.

References

SEMI C10-1109 – Guide for Determination of Method Detection Limits

SEMI C1-0310 – Guide for the Analysis of Liquid Chemicals

SEMI C36-1107 – Specification for Phosphoric Acid

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