

Application Note · novAA 800 G/D, contrAA 800 G/D



Challenge

Routine analysis of low-concentrated elements in organic solvents, shown here for copper in jet fuel

Solution

Easy and reliable analysis of organic matrices with the novAA 800 G/D and best detection limits with the contrAA 800 G/D using the graphite furnace technique

Quantification of Copper Traces in Jet Fuel according to ASTM D 6732-4

Introduction

Jet fuel or kerosene is a mixture of different hydrocarbons and typically used as fuel for gas-turbine engine powered aircrafts. Due to the variable prevalence of copper-containing alloys in manufacturing and transportation processes (e.g., pipes, brass fittings, bearings), trace level contamination of kerosene with copper (Cu) can occur. However, even ultralow levels (typically 25 µg/kg or less) of Cu in combination with the presence of oxygen and the high temperatures during combustion can catalyze oxidative degradation processes in the fuel, resulting in the build-up of insoluble residue in the engine.^[1,2] This can severely impede engine performance and seriously increase maintenance costs. Therefore, simple and reliable analytical methods are important. Since only one element needs to be investigated, albeit with very low limits of quantification, graphite furnace atomic absorption spectroscopy (GF-AAS) constitutes the best way of analyzing the copper content in jet fuel. We investigated two AAS instruments, the novAA 800 line source AAS and the continuum source contrAA 800 AAS system, both equipped with the graphite furnace atomizer and the autosampler

AS-GF. The novAA 800 offers cost-efficient and reliable measurements in this matrix without the need for special equipment. The contrAA 800 system furthermore allows to analyze the spectral surroundings of the absorption line for interferences, thus providing a holistic investigation of the measured contents, as well as offering the best performances. The measurements on both instruments will be performed with respect to the ASTM D 6732-04 norm. Due to the solvent-independent nature of GF-AAS measurements, this offers a general procedure for the analysis of trace elements in organic solvents. While the novAA 800 G and contrAA 800 G models are graphite furnace only devices, the corresponding so called Duo devices, novAA 800 D and contrAA 800 D, are equipped with the additional flame atomization technique for more flexibility in application. Thereby, applications like the determination of higher element content in gasoline, fuel, or lubricant oils in accordance to other ASTM norms are feasible.

Materials and Methods

Samples and reagents

- Jet fuel: Kerosene (low odor, Thermo Scientific)
- Oil analysis standards S-21+K (100 mg/kg Ag, Al, B, Ba, Ca, Cd, Cr, Cu, Fe, Mg, Mn, Mo, Na, Ni, P, Pb, Si, Sn, Ti, V, Zn, CONOSTAN)

Sample preparation

The line source novAA 800 G/D and the continuum source contrAA 800 G/D were used for the measurements. These devices are equipped with the autosampler AS-GF, as well as with organic solvent resistant sample cups made of PTFE (407-230.075 for 2 mL volume, 407-230.072 for 5 mL volume). Next to the graphite tubes, no further accessories or kits are necessary for the measurement of jet fuel. The instrument specific parameters of the measurements are given in Table 1, while the oven program used is shown in Table 2.

Table 1: Instrument specific parameters for the determination of Cu in jet fuel

Parameter	Specification
Device type	novAA 800 G/D contrAA 800 G/D
Tube type	Platform
Gas type	Argon
Injection sample volume	10 µL
Matrix modifier	None
Background correction	None (novAA), IBC (contrAA)
Rinsing solution	Kerosene
Wavelength used	324.7540 nm
Number of replicates	3
Number of evaluation pixels (contrAA 800 G)	3

Table 2: Applied furnace programs (same for novAA 800 G/D and contrAA 800 G/D)

Step	Name	Temp [°C]	Ramp [°C/s]	Holding time [s]	Gas flow
1	Drying	85	10	10	Max
2	Drying	100	10	15	Max
3	Drying	150	10	10	Max
4	Pyrolysis	200	25	10	Max
5	Pyrolysis	800	150	20	Max
6	Autozero	800	0	6	Stop
7	Atomize	2300	1000	8	Stop
8	Clean	2450	500	4	Max

Calibration

For the calibration of organic solvents, a mass-based approach is necessary. For that, a nominal 1 mg/kg intermediate stock standard was prepared by weighing 0.5 g of the 100 mg/kg stock standard into a suitable container and adding kerosene to yield a final mass of 50 g. The solution was ultrasonicated for 15 minutes to ensure complete mixing. The intermediate stock standard was thereafter used to prepare the calibration standards by nominally weighing 0.20, 0.40, 0.60, 0.80, 1.00, and the quality control sample by weighing 0.50 g into suitable containers respectively and adding kerosene up to 10.0 g each. The final concentrations of the calibration standards are summarized in Table 3 and the resulting calibration function for both instruments are shown in Figure 1 and 2.

Table 3: Concentrations of the calibration standards for graphite furnace technique

Standard	Concentration [$\mu\text{g}/\text{kg}$ Cu]
Cal.-Std. 0	0
Cal.-Std. 1	19.67
Cal.-Std. 2	40.57
Cal.-Std. 3	59.66
Cal.-Std. 4	80.33
Cal.-Std. 5	99.96

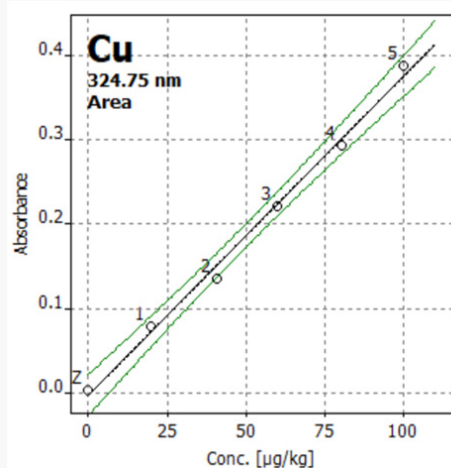


Figure 1: Resulting calibration function for Cu with the novAA 800 G. Linear, $R^2(\text{adj})=0.991$

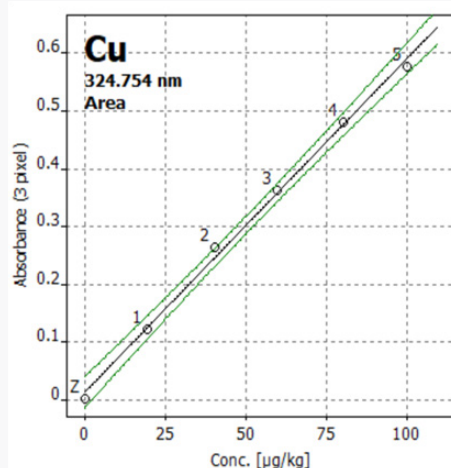
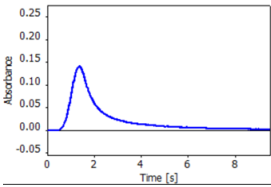
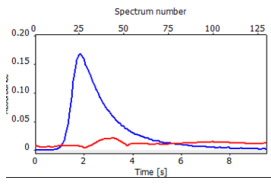
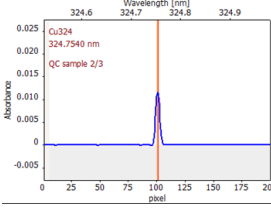
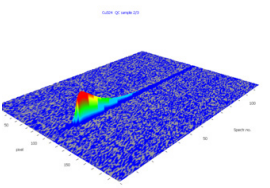


Figure 2: Resulting calibration function for Cu with the contrAA 800 G. Linear, $R^2(\text{adj})=0.995$

Results and Discussion

The measurement results of the Cu content in jet fuel are presented here. In Table 4, the typical signal shape for the measurement with the novAA 800 G/D as well as with the contrAA 800 G/D are shown. For the continuum source AAS system contrAA 800, the spectral vicinity and the 3D spectrum is shown as well. This offers helpful information with respect to possible spectral interferences, which in this case, are not present.

Table 4: Typical signals and spectral vicinity for Cu measurements

Instrument	Signal profile	Spectral vicinity	3D spectrum	Remarks
novAA 800 G (sample QC-Std. 51.33 µg/kg)		Not possible for line source AAS	Not possible for line source AAS	Background correction not necessary
contrAA 800 G (sample QC-Std. 51.33 µg/kg)				corrected with IBC

To investigate the analytical method, a separately prepared quality control sample of known concentration was measured. The respective recovery rates for the novAA 800 and the contrAA 800 instruments are shown in Table 5. The limits of detection and limits of quantification for both instruments, determined with the blank method by measuring eleven replicates, are also summarized in Table 5. The results confirm that the application can be performed with both, the classic line source AAS novAA 800 G/D as well as the continuum source AAS contrAA 800 G/D, in the latter case being slightly more accurate and sensitive.

Table 5: Analytical parameters of quality control checks

Parameter	novAA 800 G/D	contrAA 800 G/D
QC-sample concentration	51.33	51.33
Measured concentration [µg/kg]	54.79	51.58
Recovery Rate [%]	106.7	100.5
QC blank LOD [µg/kg]	0.73	0.58
QC blank LOQ [µg/kg]	2.20	1.74

QC: Quality control
LOD: Limit of detection
LOQ: Limit of quantification

Conclusion

The concentration of copper in jet fuel was investigated with graphite furnace AAS according to ASTM D 6732-04. Two different instruments were used: the classical line source novAA 800 G/D and the continuous source contrAA 800 G/D AAS system.

A linear calibration can be successfully performed for both setups using the method parameters specified in ASTM D 6732-04. The calibration is slightly better for the contrAA ($R^2(\text{adj.}) = 0.995$) than for the novAA ($R^2(\text{adj.}) = 0.991$). To investigate the quality of the method and instruments, a spiked kerosene sample was measured as a quality control. The recovery rate for the novAA was 106.7% and for the contrAA 100.5%. The limits of detection and quantification were determined with the QC blank method with 11 replicates using the calibration. In both cases, detection limits below $1 \mu\text{g}/\text{kg}$ could be achieved, whereby the contrAA again yielded slightly better values ($0.58 \mu\text{g}/\text{kg}$ compared to $0.73 \mu\text{g}/\text{kg}$). If even smaller detection limits are desired, this can easily be achieved by using a larger injection volume of 20 or 30 μL compared to the 10 μL used here. In summary, it could be shown that both instruments are well suited for the detection of copper in jet fuel, whereby the contrAA showed slightly better results across the board. Overall, both systems allow for easy and straightforward measurements of element traces in organic samples without the need for further adapting or digesting the sample. Thus, this shows the reliance and easy access of measuring organic samples with GF-AAS with the novAA 800 G/D and contrAA 800 G/D instruments. Especially with the novAA 800D and contrAA 800D, both equipped with flame and graphite furnace technique, higher element concentrations can also be analyzed using flame AAS.



Figure 3: contrAA 800D



Figure 4: novAA 800D

References

- [1] Schenk, L.; Johnson, R.; Monita, C.; Investigation of Effects of Trace Metals in the Thermal Stability of JP-7 Fuels. Southwest Research Institute. 1971, Technical Report AFAPL-TR-71-98
- [2] Doyle, A., Tristao, M.L.B., Felcman, J.; Study of fuel insolubles: Formation conditions and characterization of copper compounds. Fuel. 2006, 85/14-15, 2195-2201

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