National Laboratory of the Rockies

Current status of biodiesel metals and phosphorous test method options

Gina Fioroni and Robert McCormick



Metals and Phosphorus Methods in D6751

- EN14538 is the referee method for Na, K, Ca and Mg.
  - UOP 389 is an alternative for Ca and Mg.
  - UOP 391 is an alternative for Na and K.
- D4951 is the only phosphorus method currently listed
- Efforts to adopt D7111 are also being planned as a potential alternative for metals and P, perhaps the referee method.
  - Plans are to adopt that in conjunction with any changes needed for ULEDEs
- EN has recently adopted improvements to EN14538 that improved the r and R for Na, K, Ca, and Mg, while including P measurement

Test method

- **EN 14538:2025** - Fat and oil derivatives - Fatty acid methyl ester (FAME) - Determination of Ca, Mg, Na, K and P content by optical emission spectral analysis with inductively coupled plasma (ICP OES)

- **2nd edition of EN 14538 – first edition published in 2006**

- **Main technical modifications introduced in the 2025 version:**
  - use only kerosene as diluent
  - calibration is made with “Distilled” FAME
  - update of the precision details for Ca, Mg, Na and K following the statistical analysis of new interlaboratory tests data in accordance with EN ISO 4259-1
  - inclusion of the determination of P content with precision details obtained from the statistical analysis of new interlaboratory tests data in accordance with EN ISO 4259-1

Outcomes

- **Improved precision and lower end scope limit for Ca, Mg, Na and K compared to the 2006 edition**
- **Possibility offered to determine Ca, Mg, Na, K and P all at once**

⇒ **Possibility to specify lower and individual or combined metals limits if needed**

⇒ **EN 14538:2025 now referenced in the currently revised EN 14214 standard** (Liquid petroleum products - Fatty acid methyl esters (FAME) for use in diesel engines and heating applications - Requirements and test methods) as an alternative primary test method to measure **Group I (Ca+Mg) and Group II (Na+K) metals**, as well as **Phosphorus content**

⇒ **Could be used in D6751 as well as an option to determine P content**

Current Metals Methods – R and r

EN14538

		r	R	r	R	r	R	r	R
Element	**Scope range (mg/kg)**	**0.5 mg/kg**		**1.0 mg/kg**		**2.0 mg/kg**		**5.0 mg/kg**	
Calcium (Ca)	0,31 – 5,44	0.04483	0.17718	0.05413	0.21394	0.07273	0.28746	0.12853	0.50802
Magnesium (Mg)	0,31 – 4,57	0.02634	0.18623	0.03501	0.24749	0.05234	0.37001	0.10433	0.73757
Sodium (Na)	0,43 – 4,98	0.05300	0.22973	0.05753	0.24936	0.06659	0.28863	0.09377	0.40644
Potassium (K)	0,59 – 5,34	0.08421	0.30836	0.09351	0.34239	0.11210	0.41046	0.16787	0.61467
Phosphorus (P)	0,97 – 5,00	0,07192	0,37003	0,07192	0,37003	0,07192	0,37003	0,07192	0,37003
Ca+Mg	0,53 – 9,40	0.05603	0.27774	0.06636	0.32894	0.08702	0.43135	0.14900	0.73858
Na+K	1,05 – 9,94	0.13464	0.50227	0.14158	0.52816	0.15546	0.57994	0.19710	0.73528
Ca+Mg+Na+K	1,42 – 19,35	0.64906	0.64906	0.68216	0.68216	0.74837	0.74837	0.94700	0.94700

D4951

Element	Product	Range (mg/kg)	Precision	0.05 m%	0.1 m%	1.0 m%
Phosphorus	Oil	0.05 - 0.12	Repeatability	0.0013	0.0026	
			Reproducibility	0.0051	0.0101	
	Additive	0.7 - 1.3	Repeatability			0.041
			Reproducibility			0.149

D7111

Element	Range (mg/kg)	Repeatability	Reproducibility
Na	0.21 - 2.03	0.02916	0.2433
K	0.19 - 1.80	0.1191	0.5212
Ca	0.10 - 1.77	0.0887	0.3097
Mg	0.10 - 1.76	0.04820	0.2200
P	0.20 - 1.80	0.1396	1.3089

Metals and Phosphorus Discussion

- Are the new changes for EN14538 sufficient for metals in D6751 intended for B20/B30 use?

- Is the answer different for use in D6751 intended for B50 or B100 use as a finished fuel?

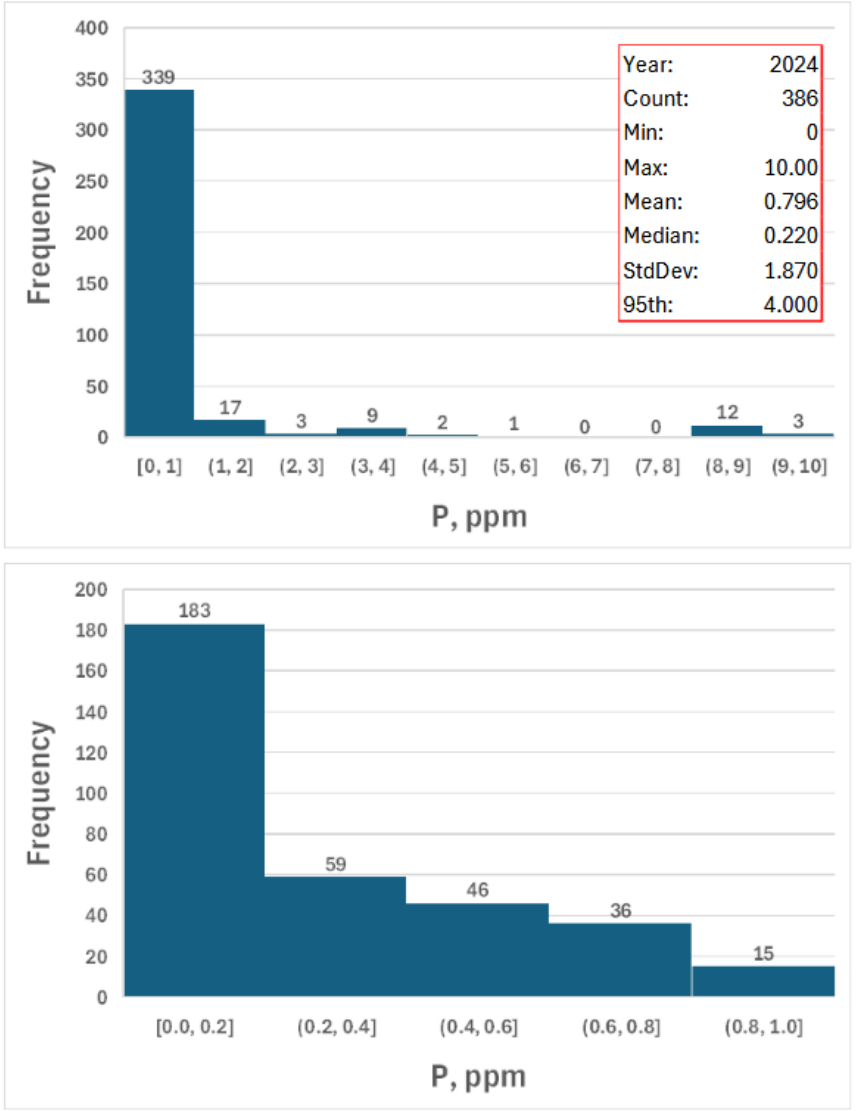
- Should D7111 be included as an alternative?
  - Used as a referee over current test methods for metals and P?

Backup Slides

2024 BQ-9000 Producer Data

Phosphorus Results from Past Surveys

- Test results were submitted by BQ-9000 companies
- Vast majority of biodiesel produced in U.S. is from BQ-9000 companies, so this essentially represents the market
- Phosphorus content for most samples was below the published detection limit of the method used. However, most producers went ahead and reported a value.



Phosphorus content of biodiesel. The top panel represents all samples, and the bottom panel for phosphorus ≤1 ppm.

2024 BQ-9000 Producer Data

