Evaluating chemical extractants to estimate available potassium for pinto beans (*Phaseolus vulgaris*) in some calcareous soils

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ABSTRACT

Evaluation of the nutrient status in soil is important for nutritional, environmental, and economical aspects. The objective of this study was to determine potassium (K) available to Pinto beans (*Phaseolus vulgaris*) in 15 soils from the Charmahal Va Bakhtyari province. The treatments included two K levels [0 and 200 mg K/kg as potassium sulfate (K₂SO₄)] and 15 soils in a factorial experiment in a randomized block design with three replications. The results indicated that in some soils K application increased yield, K concentration and K uptake by bean. The 9 extracting solutions used in this study were classified in 4 groups on the basis of the mechanism of the extraction. The first group of extractants were acidic extractants, boiling 1 mol/L HNO₃, 0.1 mol/L HNO₃, 0.1 mol/L HO₃, 0.1 mol/L HO₃, 0.1 mol/L HO₃, 0.1 mol/L HO₄, and Mehlich 1. The second group includes 0.1 mol/L BaCl₂, and 0.01 mol/L CaCl₂. The third group includes 1 mol/L NH₄OAc (ammonium acetate), and AB-DTPA (ammonium bicarbonate-diethylenetriA amine pentaaceticacid), and finally distilled water. The correlation studies showed that NH₄OAc, AB-DTPA, 0.1 mol/L BaCl₂, 0.1 mol/L HCl, and boiling 1 mol/L HNO₃ could not be used as available K extractants. But the correlation of other extractants with relative yield, plant response, concentration K, and K uptake were significant. Therefore, these extracting solutions can be used as available K extractants. Potassium critical levels by extractants were also determined by Cate-Nelson method. Potassium critical levels for 90% of relative yield were 22, 190, 28, and 50 mg/kg for distilled water, 0.1 mol/L HNO₃, Mehlich 1, and 0.01 mol/L CaCl₂, respectively.

Keywords: available K; chemical methods; bean plant; critical level

Potassium (K) is a macronutrient in plants and animals. It is also a major constituent of several soil minerals. Soil potassium (K) can be divided into four main fractions: K in soil solution; exchangeable K; non exchangeable K, which is fixed but potentially available; and K in the mineral matrix (Hoagland and Martin 1933). Higher plants draw K from the soil solution. This pool is not large enough to fulfill the need of crops in a growing season and has to be replenished by the rapidly exchangeable and slowly exchangeable forms or by fertilizer additions (Simard and Zizka 1994). Soil testing is a useful tool that can help ensure the efficient use of applied plant nutrients. Soil tests measure the quantity of a nutrient element that is extracted from a soil by a particular chemical extracting solution. The measured quantity of extractable nutrient in soil is then used to predict the crop yield response to application of the nutrient as fertilizer, manure, or other amendments. As soil test levels increase for a particular nutrient, the expected crop yield response to additions of that nutrient decreases (Haby et al. 1990). The first purpose of each extractant is the determination of available nutrients for plants. Two parameters are very important, when an extractant is utilized: (i) evaluating the nutrient labile form and (ii) extracting methods that are fast and economic (Corey 1987). The neutral 1 mol/L ammonium acetate (NH₄OAc) method, which extracts both solution and exchangeable K+ is the most common extractant in determining available potassium (Johnson and Goulding 1990). Other common extractants in determining available K in the world are Mehlich 1, Mehlich 2, Mehlich 3, ammonium bicarbonatediethylenetriamine pentaaceticacid (AB-DTPA), 0.1 mol/L barium chloride, 0.01 mol/L calcium chloride, 0.1 mol/L hydrochloric acid, boiling 1 mol/L nitric acid and distilled water (Jones 1990). Salomon (1998) compared 0.01 mol/L CaCl₂ and ammonium lactate acetic acid (common method in Sweden) and found that 0.01 mol/L CaCl2 extracted

lower K than ammonium lactate acetic acid in soil, and is a good replacement for common methods. In addition, this extractant is a good method for estimating of available K for corn. Zarrabi and Jalali (2008) used 0.025 mol/L H₂SO₄, 1 mol/L NaCl, 0.01 mol/L CaCl₂, 0.1 mol/L BaCl₂, and 1 mol/L NH4OAc in extracting available K for wheat in some calcareous soils of Western Iran. They found that 0.01 mol/L CaCl2, and 1 mol/L NaCl solutions were good extractants for available K estimation. Grzebisz and Oertli (1993) used 0.01 mol/L CaCl₂, AB-DTPA, Mehlich 1, 2 and 3, and 1 mol/L NH4OAC in extracting available K for soybean in West Switzerland soils. They found that AB-DTPA, Mehlich 3 and 1 mol/L NH, OAC extractants were good indices for K availability. Many researchers suggested various extractants for available K determination according to research sites (Csathó 1998, Salomon 1998, Sardi and Fuleky 2002, Hosseinpur and Sinegani 2004, Aramrak et al. 2007, Hosseinpur and Samavati 2008). The K availability is dependent to plant and soil types. Therefore, it is necessary to assess the ability of K extractants to predict plant-available K in a wide range of soils and plants. The purposes of this study were to compare K extractions by some chemical methods as predictors of bean-available K in a wide range of soils and to determine K critical levels by suitable extracting solutions.

MATERIAL AND METHODS

Fifteen calcareous soil samples (0–15 cm) with pH values from 7.7 to 8.1 (estimated using 2:1 soil water ratio) (Thomas 1996) and representing a wide range of organic carbon (C) (Nelson and Sommers 1996), cation exchange capacity (Sumner and Miller 1996), electrical conductivity in a 2:1 soil-water ratio (Rhodes 1996), calcium carbon-

ate (Loeppert and Suarez 1996), and clay content (Gee and Bauder 1986) were obtained from fields in different locations of the province of Charmahal Va Bakhtiari, in central Iran. The determination of K availability was estimated by the methods indicated in Table 1. Potassium, in all extracts, was determined using atomic emission spectroscopy.

Greenhouse experiment. Five kg of each soil (air dried) were put in 25 cm diameter pots, and arranged in a factorial experiment in a randomized complete block design with three replications and two rates of K applied as K₂SO₄ (0 and 200 mg/kg). To ensure sufficient supply of phosphorus (P), iron (Fe), and zinc (Zn), 100 mg/kg P as $Ca(H_2PO_4)_2$, 5 mg/kg Fe as sequestrine, and 5 mg/kg Zn as ZnSO₄ were added to soils. Four bean (var. pinto) seeds were planted in each pot after germination and after 1 week thinned to 3 plants per pot. For nitrogen (N), 60 mg/kg urea was added to the soils (30 mg/kg at planting time and 30 mg/kg 4 weeks after germination). The pots were irrigated daily, and moisture was maintained near field capacity. Ten weeks after sowing, above ground portions were harvested and prepared for analysis. Plants samples were washed with distilled water and were oven dried at 70°C with ventilation. After that, yields of dry matter were determined, and plant analysis for K was done after grinding by dry-ashing method. Plants indices including K uptake, the relative yield, and plant response were calculated by the following equations:

K uptake (mg per pot) = yield of dry matter × K concentration

Relative yield (%) = (yield of dry matter of control pots/ the yield of dry matter of treated pots) × 100 Plant response = yield of dry matter of treated pots – yield of dry matter of control pots

Statistical analysis. Correlation coefficients between K extracted by 10 extractants were determined. In addition to the selection of better

Table 1. The amount of available potassium was estimated by the following methods

Extrakt No.	Extractants	Soil-solution ratio	Equilibration time (min)	Reference
1	$0.1~\mathrm{mol/L~BaCl}_2$	1:10	30	Simard and Zizka (1994)
2	AB-DTPA	1:02	15	Helmek and Sparks (1996)
3	Mehlich 1	1:04	5	Mehlich (1984)
4	$0.01~\mathrm{mol/L}~\mathrm{CaCl}_2$	1:10	30	Salmon (1998)
5	0.1 mol/L HCl	1:10	30	Simard et al. (1991b)
6	$1~\mathrm{mol/L~NH_4OAc}$	1:10	15	Helmek and Sparks (1996)
7	$0.1~\mathrm{mol/L~HNO_3}$	1:10	30	Shivaprakash et al. (2008)
8	boiling 1 mol/L HNO_3	1:2.5	30	Al-Kanani et al. (1984)
9	distilled water	1:10	30	Mehlich (1984)

extractants, simple correlation coefficients were calculated between K extracted by chemical methods and plant indices. Finally, the K critical level for bean, for suitable extractants, was determined by the Cate-Nelson (1971) method.

RESULTS AND DISCUSSION

Some selected physical and chemical properties of the soils are shown in Table 2. Clay content ranged from 21 to 53%, CEC from 15.5 to 24.3 $\rm cmol_c/kg$, organic C content from 0.45 to 1.53%, the $\rm CaCO_3$ content from 6 to 40%, the electrical conductivity 0.11 to 0.19 ds/m, and the pH from 7.7 to 8.1.

Effects of K application on bean are shown in Table 3. Potassium application in most soils increased the dry matter yield, K uptake, and K concentration in bean significantly (P < 0.01). This parameter indicates that in some soils, bean gives a remarkable response to K application.

The mean available K of 15 soils extracted by 9 extractants are shown in Table 4 and correlation coefficients between K extracted by these chemical methods are shown in Table 5. The results show that the concentrations of K extracted varied widely with the method used, because each extractant desorbed different portions of K. Of the 9 tested methods, boiling 1 mol/L HNO $_3$ extracted the highest amount of K (mean 1543 mg/kg, ranged 740–2550 mg/kg) and distilled water removed the

lowest amount of K (mean 19.2 mg/kg, ranged 7–46 mg/kg). On average, boiling 1 mol/L HNO₃ removed 8.8, 8.9, 61.7, 5.2, 34.3, 6.7, 13.9, and 80.3 times more K than did 0.1 mol/L HNO₃, 0.1 mol/L HCl, Mehlich 1, 0.1 mol/L BaCl₂, 0.01 mol/L CaCl₂, 1 mol/L NH₄OAc, AB-DTPA, and distilled water, respectively. Liu and Bates (1990) found that the average amounts of K extracted were in ascending order: AB-DTPA < NaCl < NH₄OAC < Mehlich 3 < boiling 1 mol/L HNO₃. According to the mechanism of the extraction, these extractants were classified in four groups.

In the first group (acidic extractants), the mechanism of extracted K is displacement of K by hydrogen cation and includes boiling 1 mol/L HNO₃, 0.1 mol/L HNO₃, 0.1 mol/L HCl, and Mehlich 1. Except boiling 1 mol/L HNO₃ other extractants remove solution and slowly exchangeable K. Boiling 1 mol/L HNO₃ extracting solution, exchangeable and non-exchangeable K. The mean K of soils extracted by boiling 1 mol/L HNO₃, 0.1 mol/L HNO₃, 0.1 mol/L HCl and Mehlich 1 ranged from 740 to 2550, 78 to 329, 71 to 309 and 10 to 55 mg/kg, respectively. These results showed that K of soils extracted depends on soil and extractants characteristics. The difference of K between soils was attributed to type of clay minerals, clay and silt contents of soils. Potassium extracted by 0.1 mol/L HNO3 was significantly related to the K extracted by 0.1 mol/L HCl and Mehlich 1. Potassium extracted by boiling 1 mol/L

Table 2. Selected chemical and physical characteristics of soils studied

Soil No.	pНª	ECa (ds/m)	CEC (mmol _c /kg)	Eq. CaCO ₃ (%)	O.C (%)	Clay (%)	Silt (%)	Sand (%)
1	8.1	0.13	201	29	0.58	35	32	33
2	7.9	0.17	159	34	0.56	33	36	31
3	7.7	0.19	155	23	0.8	47	30	23
4	8.1	0.11	158	17	0.8	41	42	17
5	8.0	0.17	193	26	1.3	39	46	15
6	8.1	0.16	167	40	0.66	53	32	15
7	7.9	0.19	243	31	1.53	45	24	31
8	7.9	0.12	180	25	0.64	35	34	31
9	7.9	0.11	192	17	0.65	35	52	13
10	7.9	0.14	201	18	0.74	31	32	37
11	7.9	0.17	193	6	0.67	33	46	21
12	8.0	0.16	166	10	0.45	21	20	59
13	7.9	0.16	178	35	0.85	35	46	19
14	7.9	0.13	243	35	0.55	33	48	19
15	7.9	0.15	218	27	1.03	35	48	17

^a2:1 extract

Table 3. Effects of K application on bean dry matter, K uptake, and K concentration

Soil	Yie (g per		K concer (g/l		K uptake (mg per pot)		
No.	treated	blank	treated	blank	treated	blank	
1	6.64ª	4.85 ^a	32.9ª	21.5 ^b	218 ^a	104 ^b	
2	6.20 ^a	$5.25^{\rm b}$	23.6a	12.8 ^b	145 ^a	67 ^b	
3	7.18^{a}	7.03^{a}	30.5^{a}	19.0 ^b	219 ^a	133 ^b	
4	7.08^{a}	4.52^{b}	24.7^{a}	13.0^{b}	175 ^a	59 ^b	
5	9.10^{a}	5.40^{b}	23.5 ^a	16.0 ^b	213 ^a	87 ^b	
6	4.92a	3.60^{b}	24.4^{a}	16.9 ^b	120 ^a	61 ^b	
7	5.44^{a}	3.62^{b}	26.2a	15.6 ^b	143 ^a	57 ^b	
8	5.20 ^a	6.43^{b}	22.1 ^a	21.5 ^a	115 ^a	138 ^b	
9	5.85 ^a	4.22^{b}	24.0^{a}	14.3 ^b	140 ^a	61 ^b	
10	7.00^{a}	6.28 ^a	29.0^{a}	21.0^{b}	203 ^a	132^{b}	
11	7.55 ^a	5.67 ^b	21.5 ^a	18.0^{b}	162 ^a	102 ^b	
12	6.46 ^a	6.56 ^a	25.0^{a}	16.0 ^b	161 ^a	105 ^b	
13	3.59 ^a	4.18 ^a	29.7^{a}	25.0^{b}	107 ^a	105 ^a	
14	7.31 ^a	4.79^{b}	23.2^{a}	13.0^{b}	170 ^a	63 ^b	
15	7.02 ^a	5.25 ^b	25.7ª	10.6 ^b	181 ^a	56 ^b	

^aEach value was compared with its blank at the 0.05 level of significance

 HNO_3 was not significantly related to the K extracted by other three extractants. In the second group, the mechanism of extracted K is displacement of K by non-similar cations and includes

0.1 mol/L BaCl $_2$, and 0.01 mol/L CaCl $_2$. The mean K of soils extracted by 0.01 mol/L CaCl $_2$ and 0.1 mol/L BaCl $_2$ ranged from 14.2 to 86.4 and 251.3 to 375.0 mg/kg, respectively. As mentioned in the previous section, K of soils extracted depends on soil and extractant properties. The mean K of soils extracted by 1 mol/L BaCl $_2$ was higher than K extracted by 0.01 mol/L CaCl $_2$. This difference was attributed to concentration and Ionic radius of cations. Ionic radius of Ba $^{2+}$ is similar to K $^+$ (Ba $^{2+}$ = 0.143, K $^+$ = 0.133 and Ca $^{2+}$ = 0.099 nm), so that Ba $^{2+}$ can be easily replacement of K on exchangeable sites. Potassium extracted by 0.1 mol/L BaCl $_2$ was significantly correlated to the K extracted by 0.01 mol/L CaCl $_2$.

In the third group, the mechanism of extracted K is displacement of K by similar cation and includes 1 mol/L NH₄OAc, and AB-DTPA. The mean K of soils extracted by 1 mol/L NH₄OAC and AB-DTPA ranged from 136 to 312 and 67.0 to 165.3 mg/kg, respectively. The mean K of soils extracted by 1 mol/L NH, OAC was higher than K extracted by AB-DTPA. This difference was attributed to the concentration and time of extracting. Each two extractants contain NH₄⁺, whose ionic radius is similar to K+. These extractants desorbed solution, exchangeable and partly non-exchangeable K. Potassium extracted by 1 mol/L NH₄OAC was significantly correlated to the K extracted by AB-DTPA. Finally, distilled water extracts K from the soil solution and the mean K of soil is lower

Table 4. Amount of K (mg/kg) availability indices of the soils studied

Soil No.					Extract				
JUII INU.	1	2	3	4	5	6	7	8	9
1	273.9	113.3	26	49.0	250	231	183	1150	19
2	277.4	122.0	25	47.1	204	253	179	2100	19
3	336.5	121.0	51	92.2	252	244	285	1600	46
4	328.6	82.0	10	14.2	85	157	78	1100	7
5	265.3	104.3	13	25.8	113	223	116	2300	11
6	258.6	68.7	14	25.1	71	140	102	740	12
7	251.3	67.0	10	20.0	77	136	90	850	9
8	281.2	128.7	28	58.7	178	257	187	2200	17
9	276.7	119.3	17	33.5	131	268	140	1350	13
10	375.0	165.3	55	86.4	309	312	329	2550	37
11	359.1	127.3	23	46.4	256	274	187	1450	21
12	367.0	93.7	39	67	212	175	237	950	28
13	283.1	132.7	32	55.4	206	303	215	2450	22
14	251.6	91.0	10	18.7	79	184	104	1050	9
15	273.9	121.3	21	41.3	160	278	179	1300	18
Mean	297	111	25	45	172	229	174	1543	19.2

Table 5. Correlation coefficients between K extracted by 9 extractants

Extr.\Extr.	2	3	4	5	6	7	8	9
1	0.44 ^{ns}	0.69 ^a	0.64 ^a	0.67ª	0.28 ^{ns}	0.68a	0.17 ^{ns}	0.67 ^a
2	_	0.69^{a}	0.71^{a}	0.81^{a}	0.96^{a}	0.78^{a}	0.78^{a}	0.60^{b}
3	_	_	0.98^{a}	0.86^{a}	$0.54^{\rm b}$	0.98^{a}	0.47 ^{ns}	0.96 ^a
4	_	_	_	0.87^{a}	0.58^{b}	0.98^{a}	0.47 ^{ns}	0.96 ^a
5	_	_	_	_	0.71^{a}	0.91^{a}	0.49 ^{ns}	0.82^{a}
6	_	_	_	_	_	0.66^{a}	0.75^{a}	0.48 ^{ns}
7	_	_	_	_	_	_	0.51^{b}	0.94^{a}
8	_	_	_	_	_	_	_	0.35 ^{ns}

 $^{a}P < 0.05$; $^{b}P < 0.01$; ns not significant

than other extractants. The correlation coefficients between K extracted by this extractant and 0.01 mol/L CaCl $_2$, 0.1 mol/L BaCl $_2$, AB-DTPA, 0.1 mol/L HCl, Mehlich 1, and 0.1 mol/L HNO $_3$ extractants were significant.

The relationships between different potassium-availability indices and potassium uptake by plant are called correlation studies. In this study, plant indices including K uptake, relative yield, plant response, and K concentration were evaluated. The correlation coefficients between extracted K by 9 extractants and plant indices were shown in Table 6.

The correlation coefficients between 0.1 mol/L HNO₃, Mehlich 1, 0.01 mol/L CaCl₂, and distilled water with relative yield (0.63, 0.65, 0.70, and 0.54 respectively) and with total plant K uptake (0.80, 0.82, 0.85, and 0.75 respectively) were significantly correlated. Potassium extracted by 0.1 mol/L HNO₃, Mehlich 1, 0.01 mol/L CaCl₂, and distilled water was significantly correlated with plant indices. So it can be concluded that 0.1 mol/L HNO₃, Mehlich 1, 0.01 mol/L CaCl₂, and distilled water extractants, would be suitable as soil testing producers for determining bean available K of these soils. These results are in

agreement with those reported by Richards and Bates (1989), Simard and Zizka (1994), Hosseinpur and Sinegani (2004), and Hosseinpur and Samavati (2008). Richards and Bates (1989) found that 0.1 mol/L HNO₃ – extractable K, explained more variation in K uptake from selected Southern Ontario soils than did NH, OAC-K. Hosseinpur and Samavati (2008) found that 0.1 mol/L HNO₃, Mehlich 1, 0.01 mol/L CaCl₂, and distilled water extractants, were suitable for evaluation of K availability for corn. Also extraction methods using 0.01 mol/L CaCl₂ and 0.1 mol/L HNO₂ solutions were reported in predicting K availability to plants (Shivaprakash et al. 2008). Wanasuria et al. (1981) found that NH4OAC extractable K was not significantly correlated with rice yield response to K fertilizers. Wang et al. (2010) found that NH₄OAC method was only suitable for evaluating K availability in soils with similar K-buffering capacity, but was not suitable for evaluation of K availability in soils with different K-buffering capacities. It can be concluded that easily extractable forms of K (water soluble and easily exchangeable K play an important role in K uptake by plants. Dilute concentration of strong acid, organic acids and dilute divalent salt

Table 6. Correlation coefficient between K extracted by 9 extractants and plant indices

Extr. No.	K concentration	K uptake	Plant response	Relative yield
1	0.22 ^{ns}	0.56 ^b	-0.28 ^{ns}	0.29 ^{ns}
2	$0.45^{ m ns}$	0.64^{b}	-0.39^{ns}	0.49 ^{ns}
3	$0.54^{ m b}$	0.82^{a}	-0.64^{b}	0.65^{a}
4	0.55^{b}	0.85^{a}	-0.69^{a}	0.70^{a}
5	0.55^{b}	0.77 ^a	-0.48^{ns}	0.50^{ns}
6	0.39^{ns}	0.49 ^{ns}	$-0.34^{\rm ns}$	0.44^{ns}
7	0.52^{b}	0.80^{a}	-0.61^{b}	0.63 ^b
8	0.48^{ns}	0.57^{b}	-0.31 ^{ns}	0.49 ^{ns}
9	0.43 ^{ns}	0.75 ^a	-0.56^{b}	0.54^{b}

 $^{\mathrm{a}}P < 0.05$; $^{\mathrm{b}}P < 0.01$; $^{\mathrm{ns}}$ not significant

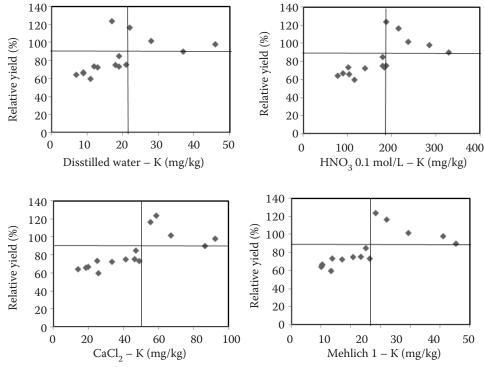


Figure 1. Cate-Nelson plot and potassium critical levels in suitable extractant

solutions are known to extract a significant part of slowly exchangeable K (Haby et al. 1990).

A good soil test should be able to predict the amount of plant-available K as well as the fertilizer responsiveness of plant growing on a wide range of soils. Predicting of plant response to fertilizers is traditionally determined by Cate-Nelson graphical method. Critical levels (CL) and Cate-Nelson plots of the relationship between the relative yield of bean and the amount of extracted K from soils by the suitable chemical methods were shown in Figure 1. The critical concentration of soil K determined by the various extraction procedures were obtained using the graphical method of Cate-Nelson and were 190, 28, 50 and 22 mg/kg for 0.1 mol/L HNO₃, Mehlich 1, 0.01 mol/L CaCl₂, and distilled water, respectively.

Over the years, many different soil testing procedures and extracting solutions were evaluated in an effort to identify a method that provides the most reliable prediction of crop yield response to nutrient application. It was determined that some soil testing procedures are best suited for particular soil types and climatic regions, whereas other soil testing procedures are better suited for different soil types and climates (Haby et al. 1990).

On average the quantity of K extracted by 9 extractants were in the following order: boiling 1 mol/L $\rm HNO_3>0.1~mol/L~BaCl_2>1~mol/L~NH_4OAC>0.1~mol/L~HNO_3>0.1~mol/L~HCl>AB-DTPA>0.01~mol/L~CaCl_2>Mehlich~1>distilled water. The$

quantity of K extracted from a soil is less important than the amount of K taken up by the actively growing plant. Traditionally in our regions available soil K is determined by extraction from soils with 1 mol/L NH4OAC that extract mainly solution and exchangeable K and a portion of interlayer K. This study shows that 1 mol/L NH₄OAC and similar extractants can not be used as available K extractants, whereas 0.1 mol/L HNO₃, Mehlich 1, 0.01 mol/L CaCl₂, and distilled water (desorbed solution and slowly exchangeable) would be suitable as soil testing methods for determining available K to bean, particularly 0.01 mol/L CaCl₂ extractant. This extractant was the best because of high correlation with plants indices. In addition, advantages of this extractant are low cost and simplicity. Further research is needed in order to test these extractants in a wide range of soils and plants and would require calibration under field conditions.

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