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SULPHUR IN THE POLISH FERTILIZATION DIAGNOSITCS

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Abstract

Over the years, researchers from Polish research centres have been improving analytical methods as well as plant and soil assays, designed to diagnose demands of crops for sulphur fertilization and to assess their supply with this element. In this article, the authors look back at the last 100 years of the Polish research on sulphur, in the context of analytical methods, soil and plant assays, and their application to assessments of crop fertilization requirements.

Studies on diagnosing crops' demand for sulphur fertilization have a long-standing tradition. Back in 1903, for example, Godlewski and Jentys wrote about nutritional demands of crops and about sulphur nutrition. For over a century since then, the analytical methods have changes, soil and plant assays have been designed and parameters have been established to facilitate assessment of plant nutrient demands. Sulphur-oxidizing autotrophic microorganisms or the fungi *Aspergillus niger* have been used for diagnosis. Another investigated possibility was monitoring the capacity of sulphur for migration, assayed in lisymetric experiments.

The 1960s were a time when modifications of earlier turbimetric methods appeared. In addition, applications of the isotope ^{35}S were checked as a sulphur marker enabling determination of the dynamics of this element in soil and in plants. With the passing of time, new technologies and measuring devices were developed. Some research centres implemented sulphur detection assays on soil and plant material with the following methods: ICP, GC, HPLC or XPF (x-ray fluorescent analysis). With respect to soil and plant tests, which admittedly are a very useful tool for monitoring the sulphur abundance in soil and nutritional demands of plants, it is now the time to state that they need further verification and calibration, in both pot and field experiments.

Key words: sulphur, fertilization demands, diagnostics, analytical methods, soil tests, plant tests.

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SIARKA W POLSKIEJ DIAGNOSTYCE NAWOZOWEJ

Abstrakt

Na przestrzeni lat w polskich ośrodkach naukowych badacze udoskonalali metody analityczne oraz testy roślinne i glebowe w celu diagnozowania potrzeb nawożenia siarką i oceny zaopatrzenia roślin w ten pierwiastek. Celem pracy była retrospektywna analiza 100 lat polskich badań nad siarką w kontekście metod analitycznych, testów glebowych i roślinnych oraz wykorzystania ich do oceny potrzeb nawozowych roślin.

Polskie badania dotyczące diagnozowania potrzeb nawożenia siarką mają długą tradycję. Już w 1903 r. GODLEWSKI i JENTYS pisali o wymaganiach pokarmowych roślin i nawożeniu siarką. W ciągu 100 lat polskich badań zmieniały się metody analityczne, opracowano testy glebowe i roślinne oraz wskaźniki mające ułatwić ocenę potrzeb nawozowych roślin. Do diagnozy wykorzystywano mikroorganizmy autotroficzne utleniające siarkę elementarną czy grzyby *Aspergillus niger*. Badano możliwości migracji siarki w doświadczeniach lizymetrycznych.

Lata 60. to zarówno modyfikacje metod turbidymetrycznych, jak i poszukiwania zastosowań izotopu ^{35}S do znakowania siarki w celu oznaczania dynamiki siarki w glebie i roślinie. W miarę upływu czasu pojawiły się nowe technologie i aparatury pomiarowe. Niektóre ośrodki naukowe zainicjowały oznaczanie siarki w materiale glebowym i roślinnym za pomocą ICP, GC, HPLC czy XPF – metodą analizy fluorescencyjnej rentgenowskiej. W nawiązaniu do testów glebowych i roślinnych, które są bardzo przydatnym narzędziem w monitorowaniu zasobności gleb w siarkę i wymagań pokarmowych roślin, można na dzień dzisiejszy stwierdzić, że wymagają one dalszych weryfikacji i kalibracji zarówno na poziomie doświadczeń wazonowych, jak i badań polowych.

Słowa kluczowe: siarka, potrzeby nawozowe, diagnostyka, metody analityczne, testy glebowe, testy roślinne.

INTRODUCTION

Sulphur is a life-sustaining element for plants, animals and people. This fact is recognized by giving it the name of a fourth macronutrient, after nitrogen, phosphorus and potassium, which is essential for plant life. At the same time, sulphur is perceived as an element degrading the natural environment, and especially in the 1990s it was seen as a noxious substance. Both excess and deficit of sulphur in nature are an unwanted development. Soil in particular, being the main store of sulphur and a source of this element for plants, should be constantly monitored with various analytical methods and tests (JAKUBUS 2006).

For years, Polish researchers have looked for more precise ways to determine concentrations of sulphur in soil and in plants. GRZESIUK (1968) wrote that ‘we lack quick and simple methods for determination of sulphates in plants. Such methods should be easy enough to make determinations even in a modestly equipped laboratory, but accurate and quick enough to serve practical diagnostic purposes for sulphur fertilization of crops.’ KOTER and GRZESIUK (1967) pointed to the fact that ‘the Polish agricultural literature does not comprise any references dedicated to some simple and accessible method for determination of sulphate sulphur in soil.’

Diagnosing the fertilization demand of soil for sulphur is not an easy task due to the dynamic and seasonal behaviour of the metal as well as its relatively high soil mobility and biochemical transformations. The aim of making a fertilization diagnosis is to estimate the current or to predict the future plant supply with a given element and, based on such information, to estimate possible yield loss or its inferior quality due to some deficit of the analyzed nutrient.

The authors' objective has been to review the last 100 years of the Polish research on sulphur in the context of analytical methods, soil and plant assays used to diagnose sulphur fertilization demand.

IMPROVEMENT OF ANALYTICAL METHODS

For many years, researchers at Polish research stations and centres have been improving analytical methods, soil and plant assays designed to assess the sulphur fertilization demand and to estimate the plant supply with this element.

Detailed methodology regarding the determination of sulphur in soil was published in 1905, in a book authored by ZYGMUNT CHMIELEWSKI, who introduced himself as 'an assistant researcher at the Experimental Chemical and Agricultural Station in Dublany.' In his publication titled A Handbook of Chemical and Agricultural Analysis, CHMIELEWSKI (1905) gave a detailed description of particular stages in determination of total and sulphate sulphur with the weight method, in which the value of SO_3 was derived from the weight of $BaSO_4$. The achieved result, he said 'gives us an idea of the general content of sulphur in the earth.'

In the 1920s, microbiological experiments were initiated on sulphur oxidation by soil microorganisms. One of the researchers involved in those investigations was OLSZYŃSKI (1927), who published a book called Sulphur Oxidation in Soil, in which he analyzed processes of sulphur oxidation in the chemical and biochemical pathway, and discussed the factors which could significantly affect the intensity of sulphur oxidation. One of the conditions which was found to have a strong effect on the rate of sulphur oxidation was the soil pH; another determinant was the type of soil in which oxidation processes occur. The aforementioned microbiological experiments together with the subsequent elaboration of their methodology had a cognitive as well as a practical value (elemental sulphur oxidation to sulphates by soil microorganisms, reduction of soil pH and its consequence such as mobilization of nutrients from soil, i.e. insoluble phosphates). Studies on sulphur oxidising soil-borne microorganisms were also pursued by KRÓL (1983), KRÓL et al. (1986), KRÓL and KOBUS (1992), who observed that stimulation of the growth of autotrophic bacteria oxidising elemental sulphur occurred only at the doses of 1.5 and 3.0 t S ha^{-1}; whenever higher amounts were applied, the counts of these bacteria declined. The above results enabled researchers to predict the capacity of microorganisms to oxidise elemental to sulphate sulphur, and to assess the abundance of sulphur in soils.

In the 1930s, physiological studies were commenced, including the uptake of sulphur by oat. An example is the experiment reported by STREBEYKO (1934), in which sulphur in plants was determined according to KÖNIG (1923). Strebeyko analysed the rate of sulphur uptake during the vegetative growth of plants. His studies showed that phosphorus nutrition had a strong influence on the uptake of sulphur, with the sulphur to phosphorus ratio being constant. This implied the parallel uptake of these two elements by plants. The physiological research translated into practical applications in the assessment of crops' nutritive demands for sulphur.

KOZŁOWSKI (1936) reports on 'a painfully felt lack of chemical analysis on mineral salt solutions from individual soil profile horizons. Any changes are closely connected to the agricultural production, therefore their recognition is of utmost importance for investigations on the productivity and fertility of soils.' The author also drew attention to analyses of soil solutions 'with strong acids, which yield „stores of elements" but have no practical value regarding any assessment of the current soil productivity or recommendations for its fertilization.' He suggested extracting fresh soil matter in distilled water, and analyzing macroelements, including sulphur, in such solutions.

In the 1960s, studies began on using the fungus *Aspergillus niger* as an indicator of the soil supplies of available sulphur. This problem was dealt with mainly by NOWOSIELSKI (1961*ab*, 1963*ab*), GÓRSKI et al. (1963). The researchers checked whether it was possible to determine total and available sulphur in soils and plants with the help of fungi called *Aspergillus niger*, comparing that method with the nephelometric one. They discovered a general proportional tendency. Overall, soils which contain much available sulphur diagnosed by nephelometry also contain much sulphur available for *Aspergillus niger*, although a reverse tendency is not repeatable. This can be explained, for instance, by the fact that the fungus is able to absorb sulphur from some organic bonds in addition to sulphate sulphur. The cited authors also emphasized the ease of conducting analyses on the quantitative determination of available forms of elements, and the higher sensitivity of the nephelometric method, which is specially important when soil contains little amounts of sulphur. Based on his studies, NOWOSIELSKI (1961) concluded that the fungus *Aspergillus niger* grows very fast and produced abundant yields of mycelium. It has high nutritional demands for agriculturally important elements. A drawback of the method based on *Aspergillus niger* was its relatively low accuracy and long duration of an analysis, typically lasting from 2.5 to 5 days. As a quantitative method, it could be applied to observations of changes in the concentration of available forms of elements; it could also be used for simultaneous assessment of the abundance of several nutrients in soil. Among the Polish researchers who examined sulphur determinations with the fungus *Aspergillus niger*, Goźliński (1970) is a good example.

Noteworthy is the broad-scale research on nephelometric sulphur determinations, completed in Olsztyn. The nephelometric method for determination of sulphur in plant extracted with 2% acetic acid designed by Grzesiuk (1968) included a simple, quick and fairly accurate technique. Koter et al. (1963) elaborated a simplified version of the Butters-Chenery's method of 1959 for determination of the soil content of sulphates in 2% solution of acetic acid. Koter and Grzesiuk (1967) adapted the method developed by Massoumie and Cornfield (1963) for determination of the soil content of sulphates in different soil solutions. The two researchers verified experimentally that 0.15% $CaCl_2$ was a suitable extraction solution for determination of water soluble sulphates; in turn, an acetate acid and phosphorus mixture could be applied in determinations of the sum of soluble and reversely absorbed sulphates. At present, sulphur determinations in soil are made with the nephelometric and turbidimetric methods, e.g. Kaczor, Brodowska (2009), Skwierawska (2008), Skwierawska (2011). A team of researchers headed Boratyński (Boratyński et al. 1975) must not be left out of our discussion. These scientists will be remembered for their methodological investigations on the analytical determination of sulphate sulphur in soil extracts with the methods by Massoumi and Cornfield (1963) as well as Bardsley and Lancaster (1960) (using a number of different extraction solutions). In conclusion, they suggested several methodological recommendations for an improved use of the two methods. They recommended the Bardsley and Lancaster's method as a simpler one and therefore more useful for series of analytical tests. The methodology of sulphur determinations with turbidimetric techniques was also examined and developed by Skłodowski (1968), who determined the content of organic sulphur with the method designed by Ewans and Rost (1945). Skłodowski modified the turbidimetric method for determination of available sulphates proposed by Ensminger (1954). Indirectly, nephelometry was also employed for determination of concentrations of glucosinolates in plants. A method was developed, which enabled determination of the total content of glucosinolates via quantitative determination of sulphur contained in sulphates generated as a product of the decomposition of glucosinolates (Krzywińska 1978). Krzywińska also worked out a modified Butters-Chenery's method and put forth her own method to determine protein sulphur in plant material (Krzywińska 1977).

In parallel, studies were conducted on the application of the isotope ^{35}S for the sake of evaluating the dynamics of sulphur transformations in soil and plants. The leading researchers in this field were Koter et al. (1965), Koter, Panak (1966), Panak (1966), Raczynskij, Panak (1966), Panak, Szafranek (1967), Panak (1970), Koter et al. (1973). For example, Koter et al. (1965) examined the use of isotope-coded sulphur in experiments on the sorption of sulphur in different types of soil. They compared extraction solutions in terms of their ability to leach sulphates from soil. Afterwards, they put the analyzed solutions in the following order: NaH_2PO_4 > $CaCl_2$ > Na_2SO_4 > H_2O. They arrived at the conclusion that $CaCl_2$ solution was best at extracting sulphates from soil, as it yielded clear and colourless extracts. PANAK (1970) used sodium sulphate tagged with the isotope ^{35}S to determine phytoavailability of sulphates from fermented manure.

Current analytical methods for determination of sulphur in soil, plants and fertilizers are described in detail by KALEMBASA (2004), who underlines that a correct sampling procedure considerably lessens analytical errors. Preparation of samples for chemical analysis can be divided into destructive and non-destructive procedures. Destructive methods involve mineralization of analyzed material, but according to a non-destructive method sulphur is determined in ground material with an elemental analysis or an XRF technique. The latter methods are distinguished by the best precision, provided the instruments are well-calibrated and operate flawlessly. KALEMBASA (2004) distinguished the following sulphur determination methods:

1. The weight method, which should be applied to samples containing large quantities of sulphur. The method consists in precipitating $BaSO_4$ and rinsing the precipitate, which is then dried and weighed.

2. The volumetric method, which takes advantage of changes in the colouration of a solution as it changes its volume. The process of sulphur determination consists of adding a known volume of barium to a solution, and titrating its excess with a titrated solution containing sulphates

3. The spectrophotometric method, which employs absorption characteristics of compounds or complexes with sulphur at an exactly set wavelength.

4. The conductometric method, which relies on the precipitation of sulphates with calcium ions in the presence of acetone. After centrifugation, the precipitate is dissolved in water and concentration of ions is measured on a conductometer.

5. The nephelometric or turbidimetric method, which measures the content of sulphur in the form of sulphates based on the turbidity of barium sulphate suspension. KALEMBASA (2004), while underlining that the method is quick and easy, adds that the final result can be affected by how fast barium chloride is added or how long the suspension is kept; in conclusion, the researcher abandons the above method for the sake of other instrumental techniques.

6. The reduction method, which means that sulphur compounds are reduced to hydrogen sulphide, which in turn is sorbed in a solution of sodium hydroxide containing bismuth. Extinction of the produced collodial bismuth sulphide is measured by spectrophotometry. The method is very sensitive and accurate, but requires corrosive reagents. It is also expensive and labour-consuming.

The instrumental methods, in which determinations can be performed in a solution, according to KALEMBASA (2004):

1. The ICO method, in which argon flows through a specially designed burner and the high temperature of plasma causes evaporation of the sample and creation of free atoms and ions. In addition, through the elimination of chemical interference, it is possible to determine other elements, and the speed and precision makes this method extremely accurate. Disadvantages of the ICP method are the high costs of equipment and occurrence of spectral interferences.

2. Ion-exchange chromatography is used for analysis of soil, plants and fertilizers.

3. The potentiometric method has found applications in the determination of total sulphur. This is a quick method and electrodes are relatively inexpensive, but the major problem is the excess of accompanying ions, sometimes appearing in quantities surpassing the amount of analyzed sulphur.

The instrumental methods in which determinations can be performed on a whole sample, according to Kalembasa (2004):

1. This method relies on the measured radiation of a sample activated with x-rays. This is a quick method, which is quite suitable for series analyses. Unfortunately, the price of an apparatus is rather high, and series of standards are needed to make analyses on soil and plant samples.

2. A CHNOS analyzer of the elemental composition provides us with a quick and clean determination method. Fully automated, this method does not call for sample preparation other than their fragmentation and drying.

3. The above list shows a wide range of analytical methods to choose from in order to determine sulphur in soil and plant material, but the actual choice depends primarily on the analytical capacity of a given laboratory.

SOIL ASSAYS

Out of a great number of analytical assays, most important are the ones which describe assimilable and available fractions of an element, which are a potential source of plant supply (Jakubus 2000).

Chemical soil tests are divided into two primary groups: extracting soluble sulphates, in which H_2O, $CaCl_2$ and LiCl are used, and adsorbed ones, mainly determined in $KHPO_4$, $Ca(H_2PO_4)_2$, NH_4OAc + HOAc extracts. In an assessment of the soil content of sulphur, sulphate sulphur has little significance as a plant available fraction due to its high changeability and dependence on environmental and agronomic factors. The soil assays which are gaining importance are the ones that also account for the content of organic sulphur, which can be transformed via mineralization into an available fraction, thus constituting one of the major sources of phytoavailable sulphur.

Available sulphur is extracted with a 0.25 M KCl solution at the temperature of 40°C for three hours (so-called KCl-40 assay). For better interpretation of results, JAKUBUS (2000, 2004*a*,*b*) distinguished the sulphate sulphur and organic sulphur fractions in the KCL-40 soil test.

A way to estimate losses of mineral components through leaching is through physicochemical soil assays, of which drainage systems and lysimeters are an intrinsic part. Based on the chemical composition of drainage waters and waters captured in lysimeters, losses of minerals leached into groundwater are assessed and a sulphur balance is made (RUSZKOWSKA 1979, PONDEL, TERELAK 1981, MOTOWICKA-TERELAK, GĄDOR 1986, GĄDOR, MOTOWICKA-TERELAK 1986, RUSZKOWSKA et al. 1988, 1993, KIEPUL 1998*a*, 1999*a*,*b*, 2007). Lysimetric experiments have demonstrated that, given the same sulphur content, plants take up more sulphur from alkaline than from acid soils. Sulphur fertilization of soils with acid reaction raises the concentration of sulphur in plants higher than identical fertilization on alkaline soils. Based on amounts of leached sulphur and potential uptake of sulphur by plants, it is possible to foresee the required sulphur fertilization.

BORECZEK (2001*a*) undertook a task to make a sulphur balance on the so called 'field surface'. The author arrived at the conclusion that the balance was negative on plots not fertilized with sulphur, and the size of a sulphur deficit depended on the uptake of this element by plants. Considering a small input of sulphur from the atmosphere, the loss of sulphates through leaching can lead to sulphur deficits on farms with intensive plant production.

PLANT ASSAYS

The visual method was mentioned back in 1903 by GODLEWSKI and JENTYS (1903). The authors gave a detailed description of crops grown on soils with controlled deficits of nutrients, suggesting that 'a deficit of just one nutrient in soil causes an inhibition – more or less severe – of the plant's development.' In 1896, GODLEWSKI and JENTYS (1903) set up a series of field experiments, including wheat, rye and potatoes, in which they analyzed the chemical composition of crops in order to determine their fertilization demand. It is a notable fact that GODLEWSKI and JENTYS (1903) did not refer to any source of methodology for analyses, but specifically named the person who completed these assays. In their article GODLEWSKI and JENTYS (1903) explained that 'the analyses were performed by Mr Konstanty Jasiński, then an assistant at the Chair of Agriculture.' They concluded that 'the supply of sulphates to potato tubers is strictly regulated by the plant's needs, because any excessive amounts of these compounds do not accumulate in tubers.' According to these authors, 'the chemical breakdown of yields can ensure more reliable clues as to the shortage or excess of plant nutrients in soil than the chemical decomposition of soil itself,' and give practical information for agriculture such as an evaluation of the soil content of nutrients. Chemical analysis of yields can provide us with valuable clues about the soil nutrient abundance, but as the above researchers stated, 'correct conclusions in this area can be drawn from quantitative ratios between these nutrients rather than from their per cent amounts (...). Thus, for improved theory of fertilization, it is extremely important that each field sampling effort generates as many chemical analyses of harvested plants as possible.'

Later REJMAN (1965) noticed that 'there is a general tendency among researchers to conduct observations on the so-called typical plants, the ones which are supposed to respond to sulphur fertilization. (...) the lack of complete studies does not facilitate any synthetic elaboration of crop requirements regarding sulphur.' Analyses of plants suffering from sulphur deficiency demonstrated that they had accumulated nitrates (V) and some non-protein nitrogen bonds. The above author highlighted the fact that plant biological assays do not allow one to draw conclusions about the absolute content of sulphur in soil.

The sulphur nutritional status of crops can be assessed visually or with plant assays. The visual method is applied to detect sulphur deficiency. Most common visual symptoms of sulphur shortage in plants are chlorosis, deformation of new leaves, decolouration of flowers and a smaller number of husks and seeds. Plants are slimmer and their growth rate is slower (KALEMBASA, GODLEWSKA 2004).Visual symptoms of sulphur deficiency can be observed on dicotyledonous plants, especially ones from the family of Brassicae (KALEMBASA, GODLEWSKA 2004). These signs include the yellowing and drying of leaves, progressing from the edge towards the centre of a leaf blade. KOTER and BENEDYCKA (1984) observed evident symptoms of sulphur deficiency in plants, which were characterized by a pale green or yellowish colour of the youngest leaves and advancing necrosis of growth apexes. In cereals, sulphur deficiency manifests itself through the formation of a field with an irregular patter of colours and structure. The gravest problem in the evaluation of sulphur deficiency in plants is the risk of erroneous interpretation. Frequently, sulphur deficiency is demonstrated analytically prior to the manifestation of visual symptoms (KALEMBASA, GODLEWSKA 2004).

Plant tests present a highly statistically verified relationship between crop yields and concentration of sulphur in plants. The most popular indicators of sulphur deficiency in plants are concentrations of sulphate sulphur, total sulphur and the value of the N:S ratio. Plant tests can be divided into biological (content of sulphates and glutathione), chemical (content of reducible sulphur) and complex assays (the N:S value and percentage of sulphate sulphur to total sulphur) (SCHNUG, HANEKLAUS 1998).

With plant tests, it is possible to determine the volume of present or to predict future deficits of some elements. Plant tests often require frequent sampling at different stages of plant development to keep abreast with dynamic changes of determined parameters. Plant tests will not help to assess the quantitative demand of crops for sulphur; they will just verify whether it is necessary to intervene by applying fast-acting fertilizers. Biological indicators are of little use to the assessment of the plant's supply with sulphur because they depend on a number of factors, for instance biotic and abiotic stresses or applied fertilization. Determination of the range of values of the total sulphur concentration in a plant enables a more precise determination of the plant's supply with this element, and for some researchers it is a better criterion for an assessment of sulphur deficiency in the plant. The N:S value is the most popular diagnostic indicator showing the plant's sulphur nutritional status. It is underlined that this ratio changes far less than other indices during the plant growing season or in response to fertilization. However, researchers argue which of the methods listed above is the best at diagnosing sulphur status (JAKUBUS 2006).

GOŹLIŃSKI (1970, 1974) designed plant tests. He highlighted the potential of complex plant tests (the N:S ratio, percentage of sulphur content) as indicators of sulphur fertilization demand. The percentage of sulphur in plant composition falling down to a certain threshold value as well as an altered N:S ratio can indicate that plants are not sufficiently supplied with this element, and therefore should be nourished with sulphur fertilizers. Similar studies on plant tests were conducted by STARZYŃSKI et al. (1974). BORECZEK (2001*b*) used plant tests to analyze the content of total sulphur and the N:S ratio in oilseed rape, wheat and maize. The plants were harvested at different stages of development according to the BBA scale and the Zadoks scale. Boreczek has concluded that the N:S ratio is a more sensitive indicator of plant nutritional status, but needs more precise calibration.

GRZEBISZ and FOTYMA (1996) evaluated the sulphur nutrition of oilseed rape grown in north-western Poland. The nutritional status of the crop was carried out according to the content of sulphur in dry matter of plants. At a low S content in dry matter (less than 0.35%) visual symptoms of sulphur deficiency appear; when the sulphur content is insufficient (0.36-0.55%), so-called hidden deficit, it cannot be detected visually. An optimal amount of sulphur in plant dry matter is 0.56-0.65%, and above it the sulphur content is high. The studies by Grzebisz and Fotyma proved that over 50% of the analyzed plantations suffered from hidden sulphur deficiency, and on fields in the former Province of Kalisz (województwo kaliskie) up to 75% of oilseed rape plantations had inadequate plant concentrations of sulphur.

The methods which determine total or sulphate sulphur content in soil and plant material are used for diagnostic purposes and for working out reports on plant fertilization needs. The diagnostic and fertilization recommendations, according to KALEMBASA and GODLEWSKA (2004), comprise three stages, of which the first one involves determinations of the content of an analyzed element in soil or in a plant, using extraction reagents for this aim. Determination of the soil content of available sulphur, that is the determination of fertilization demand for sulphur, is rather complicated and requires the use of an adequately selected extraction reagent. An assessment of the achieved results on the content of sulphur in soil or in the plant, and especially the evaluation of the methods chosen for determination of the analyzed element against threshold values, create the second stage of the process. LIPIŃSKI et al. (2003) suggested threshold values to be used by agricultural extension services. These authors analyzed concentrations of sulphate sulphur available to plants in order to estimate the soil content of this element, based on the sulphur content in soil samples. Then, they estimated the fertilization demands of crops for sulphur. An additional research tool was an analysis of linear regression. Such studies help to estimate the soil richness in sulphur and the crops' demands for sulphur fertilization, but the up-to-date results need further verification.

CONCLUSIONS AND RECOMMENDATIONS

Recapitulating, despite an obvious progress in analytical techniques and methods, it is evident that the dominant analytical method applied in the current research is the nephelometric method, originally developed by BUTTERS-CHENERY (1959), BARDSLEY-LANCASTER (1960), and EVENSA-ROSTA (1945), later modified by SKŁODOWSKI (1968), GRZESIUK (1968). Today's science takes advantage of the achievements of predecessors active in the 1960s, when a huge advance was made in terms of sulphur determinations. The sulphur determination with the *Aspergillusem niger* assay has never been implemented in a broader scale. Also, sulphur detection with the isotope ^{35}S-coded sulphur has been practically abandoned. Some research centres are now beginning to implement new sulphur analytical methods in soil or plants, such as the ICP method or the XPF x-ray fluorescent analysis, but these solutions are not popular due to the rather costly equipment they require. Soil and plant assays are a very useful tool for monitoring the soil richness in sulphur and crops' nutritional demands for this element. But these tests still need to be calibrated and verified in pot and field trials, before statistically confirmed results are available.

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