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ENHANCING THAI STUDENTS' THINKING SKILLS ABOUT ENERGY ISSUES: INFLUENCE OF LOCAL VALUES

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Abstract. The study aimed to enhance Thai students' thinking skills on learning about energy related to influence of local value. The participants consisted of 132 Grade 9 students from three different schoolsin Khon Kaen, in North East Thailand. The three participating teachers in these schools had adopted the STS energy unit that developed by researcher. The STS energy unit consists two sub-units:(1) Use energy in Thailand (issue of the increased petrol price); (2) Generation power (issue of the Mae-moh situation). Teachers had attended workshops before and during their adopting the unit. Methodology regarded interpretive paradigm. The students' thinking skills was investigated through participant observation and informal interview for ten weeks. Their thinking skills were interpreted from the orientation of their posted questions. Based on Zohar &Dori (2003) study, three question orientation attributes including phenomenon or problem description, hazards related to the problem, and treatment or solution were applied for categorized students' thinking skills. The proposing question in orientation of solution would be viewed as a higher level of understanding the problem than describing it, and finding treatment or solution was more positive and productive than just identifying hazards. Comparing between sub-unit one and two revealed that students across three schools gained more seeking practical solution to a given problem rather than being fixated on requiring about risks. Increasing the hazard and solution oriented questions indicated that the STS energy unit continually supported the development of their thinking skill classification from the sub-unit one to the sub-unit two.

*Keywords:*energy; science technology and society (STS); local value; thinking skills

Introduction

The goal of Thai science education is to assist students to develop thinking skills by considering the relationship between science, technology and society. This goal requires that people have a multidimensional scientific and technological literacy in order to make decisions about issues of science technology and society that affect living across the world (IPST, 2002). To attain the goal of science education, Thai science teachers in general agreed with the need for making science teaching more meaningful by emphasizing student-centered learning and a concern for life-long learning that should play on the relationship between science, technology and society. The goal of Thai science education was addressed along with these crucial aspects of educational reform. With the attempts for obtaining education reform, one of them involved science teaching and learning that emphasized knowledge rather than a chance for practice in analytical thinking, self-expression and acquiring knowledge by themselves.

The study of energy in Thai schools provides a good opportunity to explore how the reforms to Thai science education are being put into practice. The topic of energy raises many issues for Thailand and addressing those issues requires people who have the skills of thinking, problem-solving, and decision-making; and values that involve dealing with the interactions among science, technology, and society for local issues about energy. To solve these problems, the education reform raised crucial aspects of teaching and learning including a learner-centred approach and life-long learning. This suggests that students should have chance to be in touch and interact with all around them such as other people, nature and technology; and to apply learning methods to their real lives (ONEC, 2002).

The influences of science and technology context suggest that decision-making should be taken into account for energy learning. The decision making requires people who have higher order thinking skills to apply value judgments and other knowledge (Kortland, 1996; Bingle & Gaskell, 1994; Yuenyong & Narjaikaew, 2009). Therefore energy teaching and learning through STS approach requires students' decision making and higher order thinking skills. Term of higher order thinking skills was clarified concerning with the classical scientific inquiry skills and cognitive activities. Most of the classical scientific inquiry skills, such as formulating hypotheses, planning experiments, or drawing conclusions are also classified as higher order thinking skills. Cognitive activities involves defining the higher order thinking skills beyond the stage of understanding and lower level application according to Bloom's taxonomy. Based on Bloom's taxonomy, memorization and recall of information are classified as lower order thinking whereas analyzing, synthesizing, and evaluating are classified as higher order. Additional examples of cognitive activities that are classified as higher order include constructing arguments, asking research questions, making comparisons, solving non-algorithmic complex problems, dealing with controversies, and identifying hidden assumptions (Zohar & Dori, 2003).

This research, therefore, considers embedding cultures into studies of energy including culture of school science, communities, scientific communities, and learners in order to enhance students' thinking skills.

Entering the relationship between science, technology and society in the energy class would be a possible solution because it supports energy learning by negotiating and disputing scientific knowledge through a socialisation process (Aikenhead, 1994b). The issues about energy such as energy use, energy saving and pollution would enable students to realize the relationship between science, technology and society. The issues require students or citizens to make decisions under a framework of technological and social aspects. The social aspects involve focusing on science and technology with aspects of philosophy, sociology, history, politic, economic, and humanistic. Central to decision-making, technology is a crucial skill for citizens who need to consider multidimensional aspects in their decisions such as any social constraints (Bingle & Gaskell, 1994; Ratcliffe, 1995; Jones, 1997). Broadly speaking; technology is the ideas, designs, systems, volition of scientific applications and other knowledge that is socialised by values and norm before becoming products (de Vries, 1996; Hansen, 1997). The STS Energy teaching and learning, therefore, would allow students to learn energy through decision making for energy issues. According to the different goals of STS there are several ways of attaining STS objectives. The research emphasizes developing the STS energy unit to allow students to learn energy through solving the issues about energy regarding Aikenhead (1994a) sequence for STS science teaching. Teaching and learning is started from society realm and moved to acquiring technology, and science concepts and skills. Finally, students have chance to take action in society. Therefore, the unit should give students chances to identify problems with local interests and the impacts about energy related technological and societal issues. The Unit will, then, allow them to experience citizenship roles as they attempt to resolve issues they have identified. The framework of teaching the STS energy unit, therefore, consists of five stages: (1) identification of social issues; (2) identification of potential solutions; (3) need for knowledge; (4) decision-making; and (5) socialization stage (Yuenyong, 2006).

Identification of social issues stage

This stage is designed to focus student attention and attitudes on learning about energy. The STS instruction has to begin in the realm of society. Instruction will be begun by posing issues related to energy use in society. These questions or problems of social issues need to be solved by citizens. For energy concept, the issue of saving energy and the social problem related generating power should be brought into classroom by various strategies such as informing situation related these issues from posing in newspaper; posing the social questions related these issues for allowing students to participate in public decision-making; seeing social problem by taking field trip.

Identification of potential solutions stage

Students plan to solve the social problem related to energy use. This stage supports students to concern with the technological aspects for find the possible solutions. Technological aspects are skills to support student decision making. Students need to think of what, why, and how ideas, design, systems, volition of application scientific knowledge work for that social problems. Teaching strategies may be used discussion among students' group, role-play, brain storming, searching information via internet, and discussion with expert (e.g., engineers or scientists).

Need for knowledge stage

This stage involves developing scientific knowledge. Social questions and technological knowledge create the need to know some science content. Energy concept was formulated in many strategies to help students to understand the technology and social issues. The strategies, for examples, include reflection reading document provided by teacher, and lecture. To give feedback students' understanding about energy concept, the short quiz will be taken after class of this stage.

Decision-making stage

This stage involves student in making a decision on how to use energy knowledge and technology as solution of the social problem. This aspect public rhetoric about energy related technological and societal issues becomes dominated by dichotomies like 'chances and problem', 'advantages and disadvantages', or uses and abuses'. Student will be given chance to learn to choose between alternatives and in a thoughtful way systematically comparing as many relevant pro's and con's as possible. Teaching strategies may be used discussion among students' group, role-play, and brain storming.

Socialization stage

Students need to act as people who are a part of society by reporting their proposal for solving problem. They should also validate their solution through social process. Student might exhibit their solution in public by produce a poster, a newspaper article or a plan, social media, or present science project.

Methodology

This research is conducted regarding the interpretive paradigm. Interpretive research seeks to describe and interpret human behaviour based on their natural setting rather than form laws about it (Marriam, 1998; Cohen et al., 2000). Concerning the issue of dependability, therefore, a clear description of how data was obtained and open acknowledge of context should be taken into account. The study enters the relationship between science, technology and society in energy teaching and learning through STS approach. The research was designed to be carried out in the different school contexts in KhonKaen province including schools in the city, a small town, and a rural area. As the process of interpretation, this study aims to interpret students' thinking skills across three different schools and the implications of these for science teaching and learning in Thailand. The interpretation of data is based on fields work.

Participants

The research was carried with 132 Grade 9 students in the four different schools of KhonKaen province where located in northeastern of Thailand. These schools included school B, C, and D. Each school context is clarified as following.

School B is located in the city, KhonKaen province. The school has a total of 3,000 students in Grades 7 – 12. Kunya is the participating teacher of the school B. She graduated with a Bachelor of Education in home economics. She has 16 years of experiences teaching science. Kunya' s responsibilities include secretarial and administrative duties as well. Her participating Grade 9 science class includes 49 students, 37 girls and 12 boys, live in the city of KhonKaen and other small towns near the city of KhonKaen. Their parents work for businesses and government offices. The interesting source of energy learning in school B is the Green Classroom that provided and financially supported by the Electricity Generating Authority of Thailand (EGAT).

School C is located in a small town of the KhonKaen province where far approximately 40 km from the city of KhonKaen. The school has a total of 2,500 students in Grades 7 – 12. Ann is the participating teacher of the school C. She graduated with a Bachelor of Education in science for lower secondary school. She has 14 years of experiences teaching science. Ann' school load include not only science teaching but also working for the school academic affair. Her participating Grade 9 science class includes 47 students, 25 girls and 22 boys, who live in this small town and other villages near this small town. Their parents work in private businesses, government offices, and farms. The interesting source of energy learning in school C is the Green Classroom that provided and financially supported by the Electricity Generating Authority of Thailand (EGAT).

School D is located in a rural area of KhonKaen province where far approximately 60 kilometres from the city of KhonKaen. The school has a total of 600 students in Grades 7 – 12. Pim is the participating teacher of school D. She graduated with a Bachelor of Education in biology. She has 10 years of experiences teaching science. Pim's school load includes biology and science teaching, head of science department, and head of school academic affair. Her participating Grade 9 science class includes 29 students, 18 girls and 11 boys, who their parents work as laborers in Bangkok and as farmer. The interesting source of energy learning in the school D is the solar power pumped water that was donated by an Australian organization.

Methods of inquiry

The three participating teachers in these schools had adopted the STS energy unit that was developed by the researcher. The STS energy unit consists two sub-units:(1) Use energy in Thailand (issue of the increased petrol price); (2) Generation power (issue of the Mae-moh situation). Example of unit outlined as showing in the Table 1. Participating Teachers had attended the workshops before and during their adopting the unit. Students' posing questions in the STS energy unit could be viewed as their thinking skills classifications. The students' thinking skills was interpreted from the orientation of their posted questions.

Zohar & Dori (2003) suggested three question orientation attributes including phenomenon or problem description, hazards related to the problem, and treatment or solution. The proposing question in orientation of solution would be viewed as a higher level of understanding the problem than describing it, and finding treatment or solution was more positive and productive than just identifying hazards.

Examples of posed questions in the orientation of phenomenon include "What is the fossil?", "What is megawatt?", and "What are the effects of the Mae-moh power plant?" Orientation of identifying hazards could be seen, for examples, including "What are factors run the increased petrol price?", "If the petroleum runs out, what can we do?", "How long before will coal run out?", "How can air pollution occur at the Mae-moh?", and so on. Examples of posed question orientation of finding treatments or solutions include "What are any strategies to decrease the price of petrol?", "Are the vegetable oil used in a car?", "What can we do to reduce the use of coal?", and "Why doesn't government construct the Nuclear power plant?"

Table 1. Example of outline of the STS energy lesson plan

Sub-units	Issues	Activities
2. Generation power (8 sessions)	How can we find the solutions for the demand in electric energy and the problems of the power plant that polluted the air?	<u>Identification of social issues stage:</u> ● Brain storming to make the sceptical ideas about the Mae-moh power plant situation. ● Conclude and categorize trends of question orientation. <u>Identification of potential solution stage:</u> ● Brain storming for possible alternative solutions of each oriented question category ● Clarify the related knowledge known and unknown <u>Need for knowledge stage:</u> ● Do experiment of electromagnetic induction with the simple dynamo ● Do experiment of electromagnetic induction with a simple dynamo ● Study the process of generation power in hydro and coal fire power plants ● Num-pong power plant trip to attend engineer power plant conversation. <u>Decision making stage</u> ● Plan and search more information for the role-play of the Mae moh situation. ● Collect the background information to think of what and how will be the best volition of the Mae-moh situation <u>Socialization stage:</u> ● Organize role-play of the Mae-moh situation as public hearing. ● Num-pong power plant trip to share engineer some alternative solution for the power plant that pollute the air.

Findings

The STS energy unit gave students chance to make skeptical ideas to the energy issues related technological and societal aspects. Students' posing questions could be viewed their thinking skills classifications. The number of posed questions in the Identification of social issues stage was counted and categorized each question by its orientation. Students' thinking skills in school B, C, and D could be reported as below.

School B students' thinking skills

Students' posing questions showed their thinking skills classifications. The number of posed questions in the Identification of social issues stage was counted and categorized each question by its orientation. The three question orientation attributes include phenomenon or problem description, hazards related to the problem, and treatment or solution. The proposing question in orientation of solution would be viewed as a higher level of understanding the problem than describing it, and finding treatment or solution was more positive and productive than just identifying hazards.

In sub-unit one, school B students developed their understanding the issues through group discussion. Then they posed their question to the issue of increased petrol price. Interestingly, all groups of students posed a number of oriented questions of finding treatments or solutions. There were not many the oriented questions of phenomenon and identifying hazards as showed in the Fig. 1. Examples of posed questions in the orientation of phenomenon include: what is the fossil; what is the difference of benzene 91 and 95?

Examples of posed question orientation of identifying hazards in sub-unit one include: what are factors run the increased petrol price; if the petroleum runs out, what can we do; if the government did not fix the petrol price, how will the economic be ruined now.

Examples of posed question orientation of finding treatments or solutions in sub-unit one include: what are any strategies to decrease the price of petrol; what don't we use other energy sources e.g., wind and water power to substitute petrol; if the petrol price keeps growing, shall we use some renewable energy sources; what are the energy sources that should be substituted the petrol; are the vegetable oil used in a car.

In sub-unit two, again, school B students posed a number of questions of solution orientation. There were not many the oriented questions of phenomenon and identifying hazards as showed in the Fig. 1. These assumed that they held a high level of thinking skills classifications. The examples of posed questions in the orientation of phenomenon include: what is megawatt; what are the effects of the Mae moh power plant.

Examples of posed question orientation of identifying hazards in sub-unit two include:How long before will coal run out; How can air pollution occur at the Mae-moh; why did air pollution surrounding the Mae moh power plant turn to be serious in the winter.

Examples of posed question orientation of finding treatments or solutions in sub-unit twoinclude:What can we do to reduce the use of coal; Why don't they use other energy sources; why doesn't government construct the Nuclear power plant; what are the strategies that should be used to eliminate the sulfur dioxide; what should we do next to solve the problem of the Mae-moh environment damages.

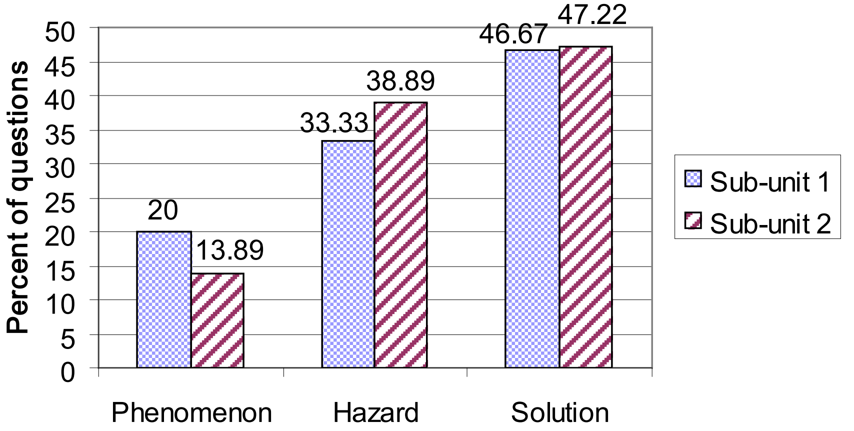

Fig. 1. Trends in the School B students' question orientation of the sub-unit 1 and 2

According to Fig.1, the STS energy unit exposed students to controversial energy issues that allowed students to express their ability of thinking skills classifications. Approximately fifty percent of school B students' posing the solution oriented questions was found both in sub-unit one and two. The percentages of identifying hazards oriented questions increased from 33.33% in sub-unit one to 38.89% in sub-unit two. The percentages of phenomenon oriented question decreased from 20.00% in sub-unit one to 13.89% in sub-unit two. This suggested that the STS energy unit continually supported the development of school B students' thinking skill classification from sub-unit one to sub-unit two.

School C students' thinking skills

Students' posing questions could analyze their thinking skills classifications. The number of posed questions in the Identification of social issues stage was counted and categorized each question by its orientation. The three question orientation attributes include phenomenon or problem description, hazards related to the problem, and treatment or solution. The proposing question in orientation of solution would be regarded as a higher level of understanding the problem than describing it, and finding treatment or solution was more positive and productive than just identifying hazards.

School C students were, the first sub-unit, a little confused why they needed to pose questions. They seemed to be worried the answer of those questions. They had to know what they asked. They, therefore, normally posed questions that were provided information in worksheets. Posed questions in sub-unit one were categorized into the orientation of phenomenon or problem description, for examples: what is fossil; how many bath has government paid to fix price of petrol below 20 bath per liter; what year did we encounter with the situation of high petrol price.

The examples of posed question orientation of identifying hazards in sub-unit one include: when will the price of petrol be higher than 20 bath per liter; what happen next, if the government stops paying money to fix oil price.

The examples of posed question orientation of finding treatments or solutions in sub-unit one include: what can we do to decrease energy use; what should we do when the oil run out.

Starting sub-unit 2, students felt free to pose questions. It was observed that they tried to pose more question. They shared their skeptical ideas of the Mae-moh situation in group. Their questions posed in sub-unit two were categorized into the orientation of phenomenon, for example: what province was the Mae-moh power plant located; how many watts does one megawatt equal; what is the chemical formula of sulfur dioxide; what fuel was used in Mae-moh; what happened in the year 1987 and 1997.

The examples of posed question orientation of identifying hazards in sub-unit two include: how did emitted sulfur dioxide affect the environment; what are kinds of diseases that are caused by the sulfur dioxide; how can air pollution occur at the Mae-moh; what are disadvantage consequences of closing down the Mae-moh power plant.

The examples of posed question orientation of finding treatments or solutions in sub-unit two include: what should be the fuel of the Mae-moh power plant, if the lignite was used; if you were in this situation, what would you do; what should be the method of emitting gas from the power plant for reducing environment damages as much as we could; what should we do next to solve the problem of the Mae-moh environment damages.

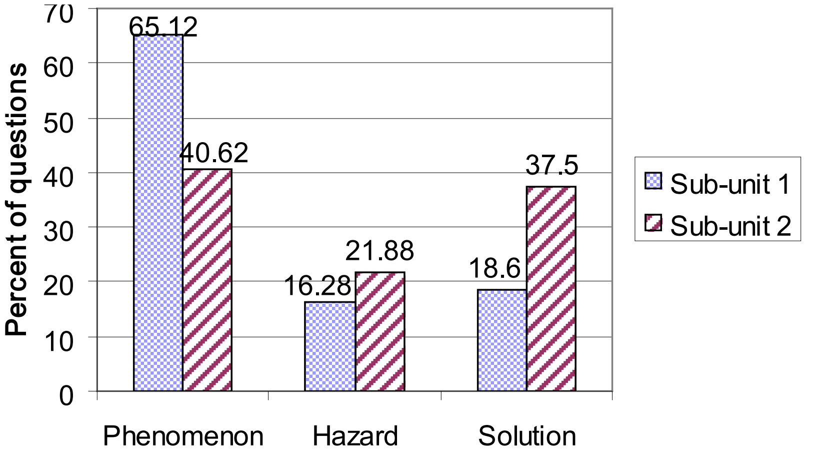

Fig. 2. Trends in the school C students' question orientation of sub-unit 1 and 2

Compare trend of students questions' orientation between sub-unit 1 and 2. According to Fig. 2, the percentage of phenomenon oriented question decreased from 65.12% in sub-unit 1 to 40.62% in sub-unit 2. The percentages of solution and hazard oriented questions increased from 18.6% in sub-unit 1 to 37.5% in sub-unit 2, and 16.28% in sub-unit 1 to 21.88% in sub-unit 2; respectively. This indicated that students expanded higher level of thinking skills. Huge increase in solution oriented questions indicated that students aware of seeking practical solution to a given problem rather than being fixated on requiring about risks. This suggested that considering the alternative solution in sub-unit one stimulated students to develop their thinking skill classifications in the beginning of sub-unit two.However, the phenomenon oriented questions still remained the highest number of questions. This might root from students posing questions of which they had already known the detailed information answer. They seemed to be worried about the answer of their questions.

School D students' thinking skills

Students' posing questions could analyze their thinking skills classifications. The number of posed questions in the Identification of social issues stage was counted and categorized each question by its orientation. The three question orientation attributes include phenomenon or problem description, hazards related to the problem, and treatment or solution. The proposing question in orientation of solution would be considered as a higher level of understanding the problem than describing it, and finding treatment or solution was more positive and productive than just identifying hazards.

In sub-unit one, school D students developed their understanding of issues through group discussion. Then they posed their question to the issue of the increased petrol price. It seemed that they tried to make the questions from the provided information rather than from their skeptical views. This resulted that there were a number of posed questions in the orientation of the phenomenon or problem description but there were few posed questions in the orientation of the identifying hazards, and the finding treatments or solutions as showed in the Fig.3. The examples of posed questions in the orientation of phenomenon include: how much has the government paid for fixing the petrol price since the 10th January until 17th June 2004; what does the word of the fixing the petrol price mean; how does the petrol involve the oil; where oil discovered first.

The examples of posed question orientation of identifying hazards in sub-unit one include: if the government does not longer fix the petrol price, how will Thailand economic be; the increased petrol price affects the goods price and cost of electricity - so, what is next; if the government does not longer fix the petrol price, what will be happened.

The examples of posed question orientation of finding treatments or solutions in sub-unit one include: if oil runs out, what energy sources should be substituted.

In sub-unit two, Teacher Pim reflected students to make questions requiring analysis or applications. She reminded her students to decrease the questions that had explicitly known answers. This fostered the school D students to make a number of the questions in the orientation of the hazards and the solutions as shown in Fig.3. School D students posed the question orientation of phenomenon in sub-unit two, for example: what are the causes of the 1st – 3rd the Mae-moh power plant generator stopped running; how many megawatts does a generator produce; how many years have the Mae-moh power plant run.

The examples of posed question orientation of identifying hazards in sub-unit two include: what are the environment effects of sulfur dioxide; why does the Mae-moh power plant hurt a number of people surrounding the Mae-moh district; mae-moh power plant released sulfur dioxide polluting the air; what else pollutes the air; if we have no longer the Mae-moh power plant, how will we have enough electric energy use.

Examples of posed question orientation of finding treatments or solutions in sub-unit two include: how can the government solve the problem of the Mae-moh situation; if the coal runs out, what energy sources should be used; what other energy sources should be used in the Mae-moh power plant; how will we protect and solve the problem of air pollution; what are the strategies that should be used to eliminate sulfur dioxide.

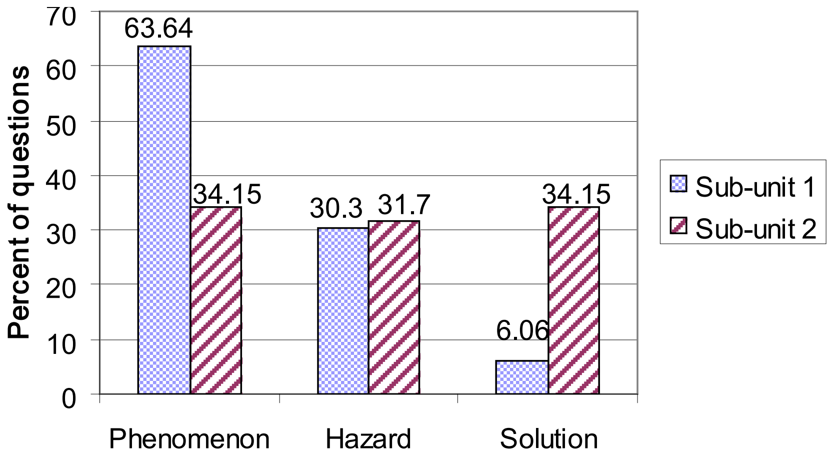

Fig. 3. Trends in the school D students' question orientation of the Sub-unit 1 and 2

According to the Fig. 3, it assumed that the STS energy unit exposed students to controversial energy issues that advocated students to develop their ability of thinking skills classifications. The percentages of phenomenon oriented question decreased from 63.64% in sub-unit one to 34.15% in sub-unit two. The percentages of hazard oriented questions stay quite the same. The percentages of solution oriented questions increased from 6.06% in sub-unit one to 34.15% in sub-unit two. A Huge increase of the solution oriented questions indicated that school D students expanded higher level of thinking skills. They gained more seeking practical solution to a given problem rather than being fixated on requiring about risks. This suggested that the STS energy unit continually supported the development of school D students' thinking skill classification from sub-unit one to sub-unit two.

Conclusion

This study indicated the strengths of energy teaching and learning through the STS approach. The STS energy teaching and learning not only enhanced students' understanding of energy concepts but also gave students chances to develop their thinking skills.Comparing between sub-unit one and two revealed that students across three schools gained more seeking practical solution to a given problem rather than being fixated on requiring about risks (Figs. 1-3). Increasing the hazard and solution oriented questions indicated that the STS energy unit continually supported the development of their thinking skill classification from the sub-unit one to the sub-unit two. Interestingly, there was a huge of an increase solution oriented question for school C and D students. This assumed that they expanded a higher level of thinking skills classification. This reflected also that number of them had a lower level of thinking skills before the STS energy unit. Therefore, it assumes that the STS unit could enhance students to develop their thinking skills although they came from different background and prior knowledge.

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LIQUID-LIQUID EXTRACTION AND SPECTROPHOTOMETRIC CHARACTERIZATION OF SOME NEW ION-ASSOCIATED COMPLEXES OF Co(II) WITH INT: APPLICATION OF THE DEVELOPED METHOD FOR ANALYSIS OF SOIL COBALT CONTENT

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Abstract. The study presents a newly-developed method for extraction-spectrophotometric determination of Co(II) in samples by means of iodnitrotetrazolium chloride. The electronic spectrum of cobalt ion associated has a peak at 630 nm. At that wavelength the absorption is maximum. The ratio INT: $[Co(SCN)_4]$ in the triple ion-associate complex was 2:1, and due to the good solubility of the Co(II) ion associated and INT in 1,2 dichloroethane, maximum extraction in the organic phase was achieved after 30 s extraction. The molar absorptivity of the studied ion associate $INT_2[Co(SCN)_4]$ was $\varepsilon_{630} = 0.6\times10^3$ dm^3 mol^{-1} cm^{-1}. Sendel's sensitivity of the method was 9.8×10^{-2} mg cm^{-2}. The maximum quantity of Co extracted with INT was achieved at pH 2-7. The relationship between Co(II) concentration and absorption was linear in the range of 6 – 125 mg Co(II) in 10 cm^{-3} aqueous solutions.

Keywords: Co; determination; INT; soils; spectrophotometry

Introduction

It is widely known that Co content in agrochemical objects is insignificant (Sandell, 1959; Meyers, 2000; Cucinotta et al., 2008; Makarova & Kupalina, 2015; Toncheva et al., 2016; Çiftci et al., 2009). The scientific literature presents many methods for separation, preconcentration and determination of cobalt in samples (Makarova & Kupalina, 2015; Toncheva et al., 2016; Tewari, 2009; Sabil et al., 2009; Pouretedal et al., 2009; Çiftci , 2010; Berton & Wuilloud, 2011; Boggs et al., 2012; Divarova et al., 2013). The widely applied methods for determination of the element content are photo colorimetric, polarographic and spectral. Extraction-photometric methods are applied for determination of ultra-small Co quantities in agrochemical objects. Their major advantages are simplicity, rapidity and accessibility. In the analytical practice, the reaction between Co(II) and nitroso-R-salt is widely used. One of the base factors that reduces the precision of the photometric determination of Co micro quantities in soil samples is the presence of colored organic compounds, as well as Fe, Ni and Cu salts.

Till now literature presents only a few methods for Co determination in soil and plants. The following reagents are used: 1,10–phenantrolyne and eozine, thiodibenzoylmethane, picraminazo-4-cyclohexilrezorcine, diantipirilmethane, 2-(2-benzthiazolylazo)-5-dymethilaminobenzoic acid. Some of these methods require exact working pH and preliminary samples staying before Co determination. Other methods characterize with low sensibility and selectivity. Another method for quantitative determination of Co includes heating to 80^{o} C. Besides, the complex formed is stable for only 20 min.[1-13]

The aim of the present study was the development of extraction-spectrophotometric method for Co(II) determination in soils, with selectivity and expressivity exceeding most of the up-to-date applied methods. The structure formula of INT is presented in Fig. 1.

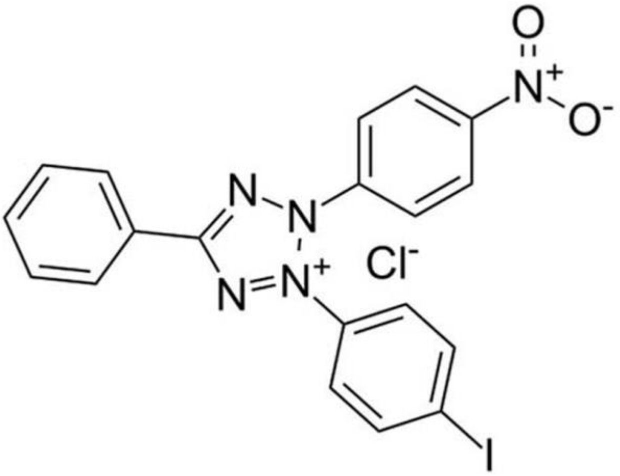

Fig. 1. Structure formula of INT (IUPAC name: *3-(4-Iodophenyl)-2-(4-nitrophenyl)-5-phenyl-2H-tetrazol-3-ium chloride;* Other names: *2-(4-Iodophenyl)-3-(4-nitrophenyl)-5-phenyltetrazolium chloride; Iodonitrotetrazolium chloride*, *INT*

For accomplishment of this goal the following objectives should be fullfilled: (I) to investigate the solubility of the ion-associated thiocyanate complex of Co(II) with iodnitrotetrazolium chloride (INT) in different organic solvents, to select the most appropriate of them; (II) to study the effect of pH; (III) to investigate the time necessary for Co extraction, and to estimate the time necessary for full metal extraction in organic phase in the form of ionic associate; (IV) to study the effect of the concentrations of the reagents participating in the extraction equilibrium of the system: the optimal established quantity of each of them would guarantee full extraction of Co(II) in the investigated monotetrazolium salt; (V) to assess the selectivity of the developed method towards side ions, their effect on the Co extraction and determination has to be analyzed.

Materials and methods

Apparatus

Absorbance measurements were made on a UV - VIS spectrophotometer, Germany, with a 1 cm quartz cuvette, 630 nm.

Reagents

The reagents applied were of analytical grade (p.a. Merck and Fluka).All solutions were prepared with distilled demineralized water.

Extraction procedure

In a separating funnel of 100 ml the following solutions: 1 cm^{-3} Co(II) 1×10^{-3} mol dm^{-3}, 1 cm^{-3} 4 mol dm^{-3} potassium thiocyanate, 7 cm^{-3} iodnitrotetrazolium chloride (INT) 1.5×10^{-3} mol dm^{-3} were added. Distilled water was added to the water phase to 10 cm^{-3}volume. The following step was extraction with 3 cm^{-3} 1,2-dichlorethane for 30 s. After delamination of the two phases, the organic phase was transferred through a paper filter into a cuvette b = 1 cm and subjected to photometric analyzes at 630 nm on UV - VIS spectrophotometer.

Results and discussion

Optimal condition

The extraction of the Co ion associate in different organic solvents: methyl ethyl ketone, 1,2-dichlorethane, chloroform, benzene, toluene, tetrachloromethane and diethyl ether, was studied.

The most appropriate organic solvent was chosen on the base of these investigations. 1,2-dichloroethane was the most suitable. The electronic spectrum of the cobalt ion associate had a maximum at 630 nm (Fig. 2). The maximum absorption was detected at this wavelength.

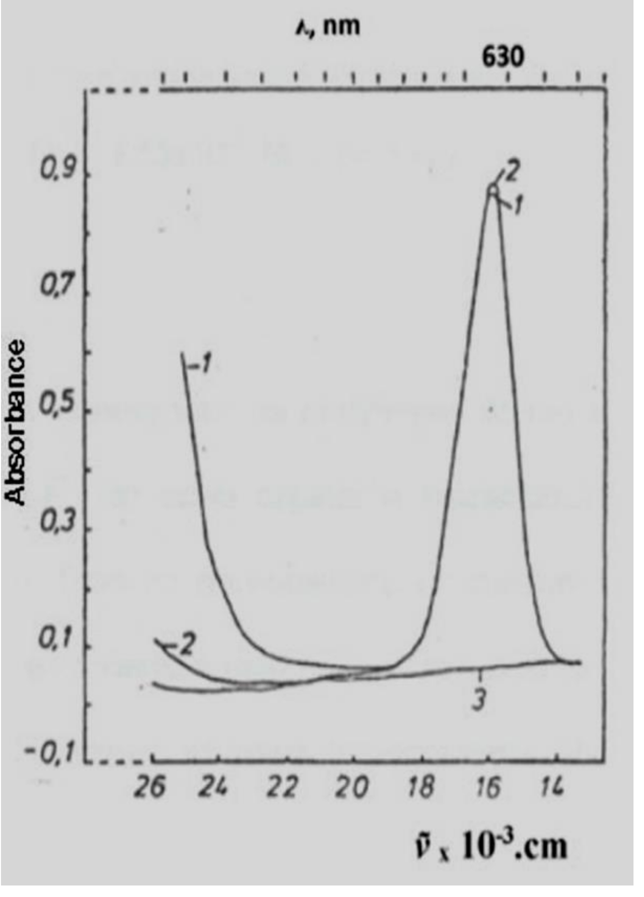

Fig. 2. 1 – Electron spectrum of $INT_2[Co(SCN)_4]$ in methyl ethyl ketone. Concentrations in the aqueous phase before extraction:$C_{Co(II)} = 8.25\times10^{-4}$ mol dm^{-3}, $C_{INT} = 1.65\times10^{-3}$ mol dm^{-3}, $C_{SCN} = 0.67$ mol dm^{-3}, b = 1 cm; 2 – Electron spectrum of $[Co(SCN)_4]^{2-}$ in methyl ethyl ketone. Concentrations in the aqueous phase before extraction: $C_{Co(II)} = 8.25\times10^{-4}$ mol dm^{-3}, $C_{SCN} = 0.67$ mol dm^{-3}, b = 1 cm; 3 – Electron spectrum of INT in dichloroethane. Electronic spectrum of INT in dichloroethane. Concentration in the aqueous phase before extraction of INT – 1.65×10^{-3} mol dm^{-3}, b = 1 cm

The bond in the molecule of the obtained ion associate, formed $[Co(SCN)_4]^{2-}$ and the tetrazolium salt was electrostatic. This was confirmed by the electronic spectra readings of the ion associate, and those of the constituent components (Fig.

2). Studies had shown that there was no shift in the absorption bands of the compounds. The spectra of the three-ion-associated complex and the thiocyanate complex ion had absorption bands at the same wavelength. This indicates that the bond is not coordinative.

Composition of the triple ion-associated complex

The composition of the triple ion-associated complex was proven by the Ostromislensky – Job method (Bulatov & Kalinkin, 1972). The present investigation displayed that the relationship INT: $[Co(SCN)_4]$ was 2:1 (Fig. 3).

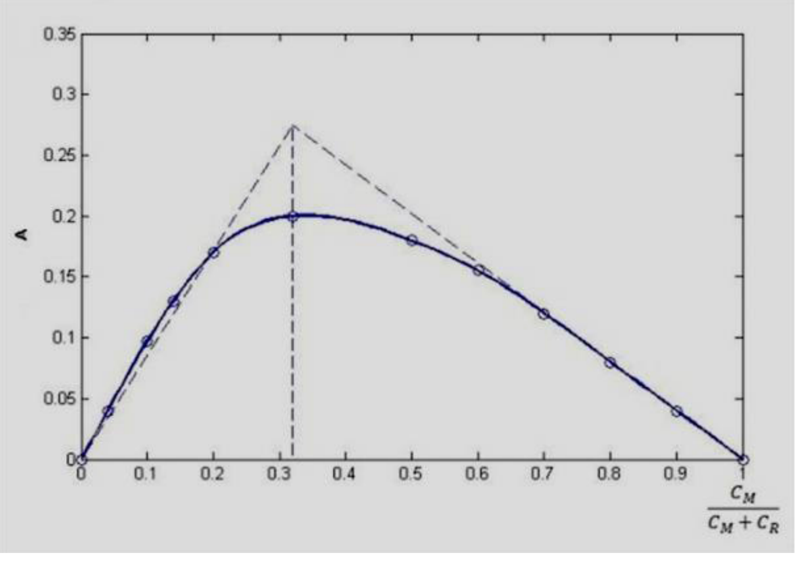

Fig. 3. Graphical determination of the molar ratio of the complex $INT_2[Co(SCN)_4]$ according to Ostromislensky – Job method: C_{SCN} = 0.67 mol dm^{-3}, b = 1 cm, l_{max} = 630 nm

Extraction time

The effect of time as a factor for achieving extraction equilibrium between the two phases was studied. Due to the good solubility of the ion-associated complex of cobalt (II) and INT in 1,2-dichloroethane, maximum extraction of the organic phase was obtained at 30 s extraction (Fig. 4).

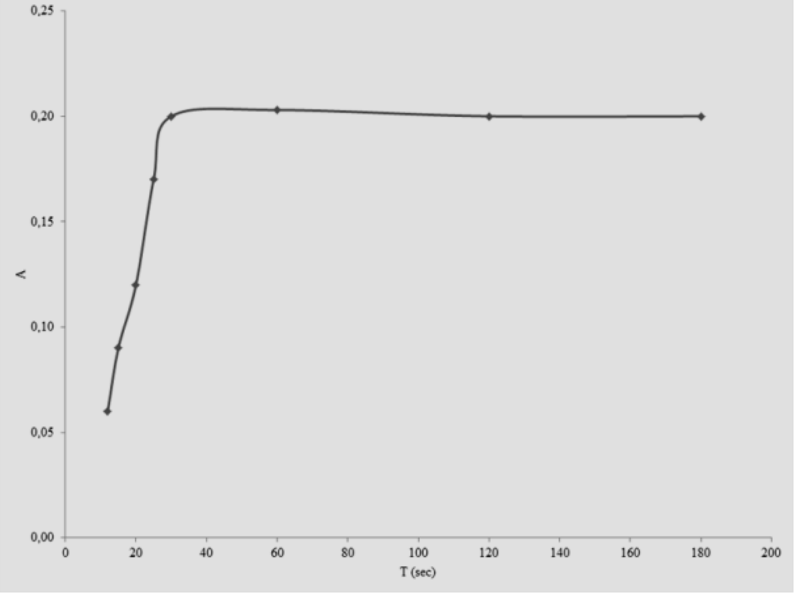

Fig. 4. Relationship between the change of light absorption and extraction time of the complex $INT_2[Co(SCN)_4]$: $C_{Co(II)} = 1\times10^{-4}$ mol dm^{-3}, $C_{INT} = 4\times10^{-4}$ mol dm^{-3}, $C_{SCN} = 0.8$ mol dm^{-3}, b = 1 cm

Determination of the molar absorbance of the ion triple associated thiocyanate complex of cobalt (II) and INT

Molar absorbance of the ion associate $INT_2[Co(SCN)_4]$ was determined by the method of Komar-Tolmachov (Bulatov & Kalinkin, 1972). The molar absorbance was determined by measuring of the light absorbance of solution with different concentration of the reagents at constant stoichiometry. The data from the experimental analyzes are presented in Table 1.

Table 1. Determination of the molar absorptivity of the ion-associated complex

Co(II) - 1.10^{-3} mol dm^{-3}	$C_{Co(II)}$	A	C.l / A = ε^{-1}	10^{-3}. ε^{-1}	$1/\sqrt[n+1]{A^n}$
0.1	0.00001	0.020	0.0005	0.50	7.09
0.2	0.00002	0.030	0.0007	0.76	5.78
0.8	0.00008	0.080	0.001	1.00	3.78
2	0.0002	0.160	0.00125	1.25	2.67

The molar absorbance of the studied ion associate $INT_2[Co(SCN)_4]$ was e_{630} = 0.6×10^3 dm^3 mol^{-1} cm^{-1}. The sensitivity of the method according to Sendel [1] was 9.8×10^{-2} mg cm^{-2}.

Study of the medium acidity

The acidity of the medium is a factor that affects the amount of cobalt uptake by the organic phase. Fig. 5 illustrates the influence of pH of the aqueous phase on the change in light absorbance of the test solution. There is a very large pH range in which it has constant values. Experimental data showed that light absorption of neutral and acidic medium to pH 2 has a constant (maximum) value. At pH < 2, it begins to decrease and the determination becomes impossible. Maximum Co(II) uptake was achieved at pH 2-7 range. The too large pH range makes it possible to work without precisely controlling the pH, or to use buffer solution. This makes the method less pretentious.

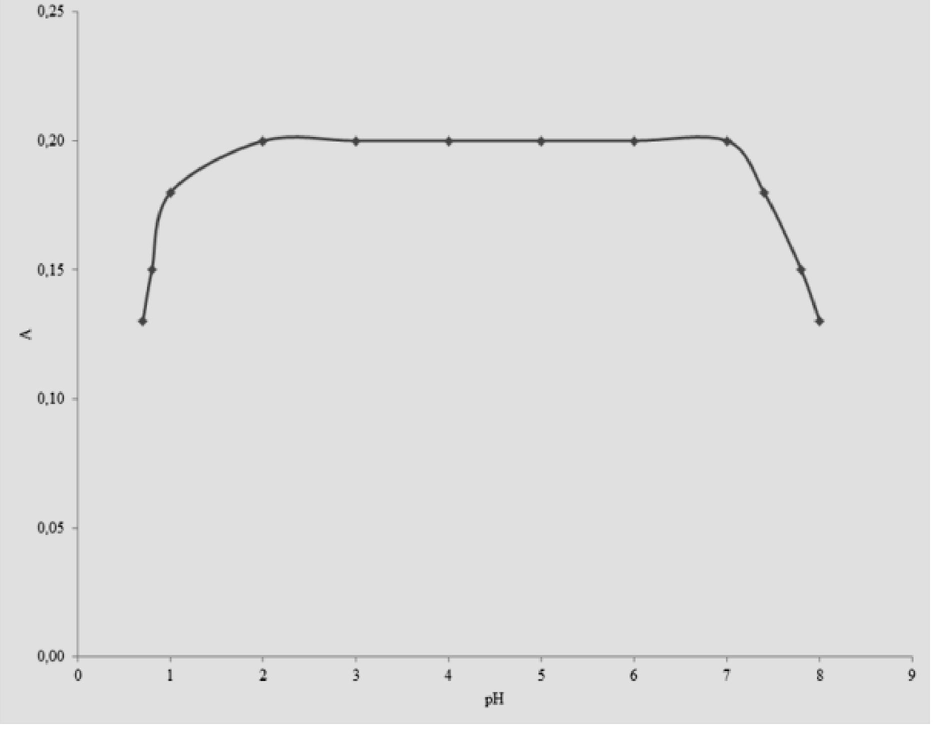

Fig. 5. Effect of pH on the light absorption during Co(II) extraction with INT.
$C_{Co(II)} = 1\times10^{-4}$ mol dm^{-3}, $C_{INT} = 4\times10^{-4}$ mol dm^{-3}, $C_{SCN} = 0.8$ mol dm^{-3}, b = 1 cm

Reagents quantity

To develop optimal conditions and extraction of the thiocyanate complex of Co(II) with INT the influence of the tetrazole salt and thiocyanate ions was examined. The formation of the ion associate significantly depends on the concentration of the thiocyanate ions. In order to shift the equilibrium to the formation of the thiocyanate complex of Co(II) an excess of thiocyanate ions was required. This excess had no effect on the extraction equilibrium and facilitated the quantitative extraction of cobalt in the organic phase. By varying the amount of thiocyanate ions was found that at a concentration of ≥ 1 mol dm^{-3} in the water phase, the light absorbance of the extracts was the highest (Fig. 6).

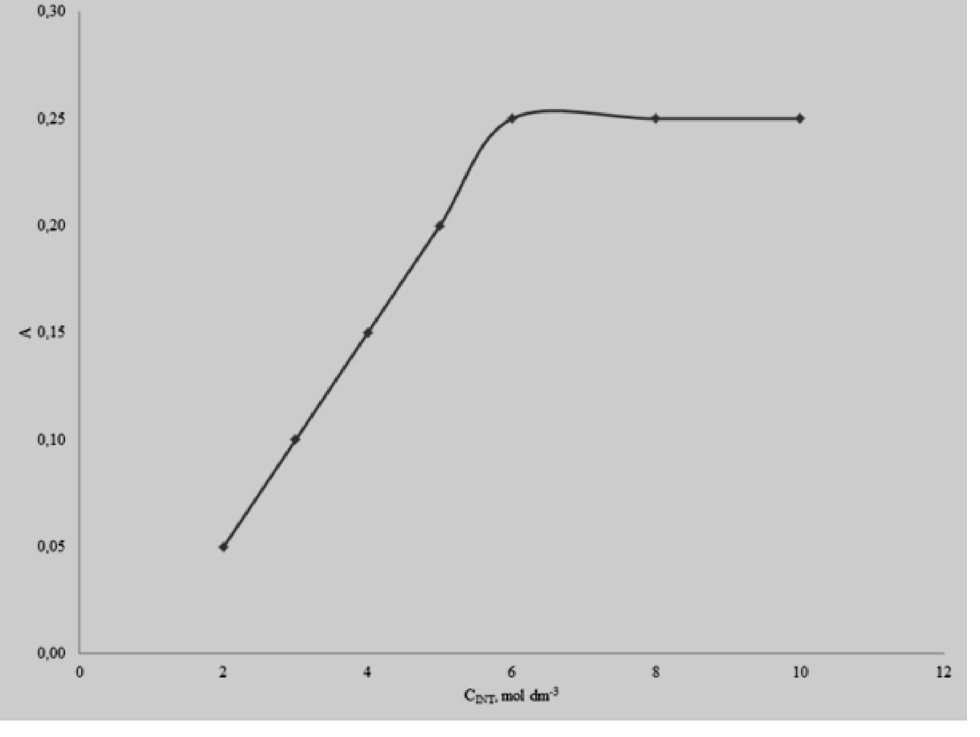

Fig. 6. Relationship between the change of light absorption and SCN^- ions concentration:
$C_{Co(II)} = 1\times10^{-4}$ mol dm^{-3}, $C_{INT} = 3\times10^{-4}$ mol dm^{-3}, b = 1 cm

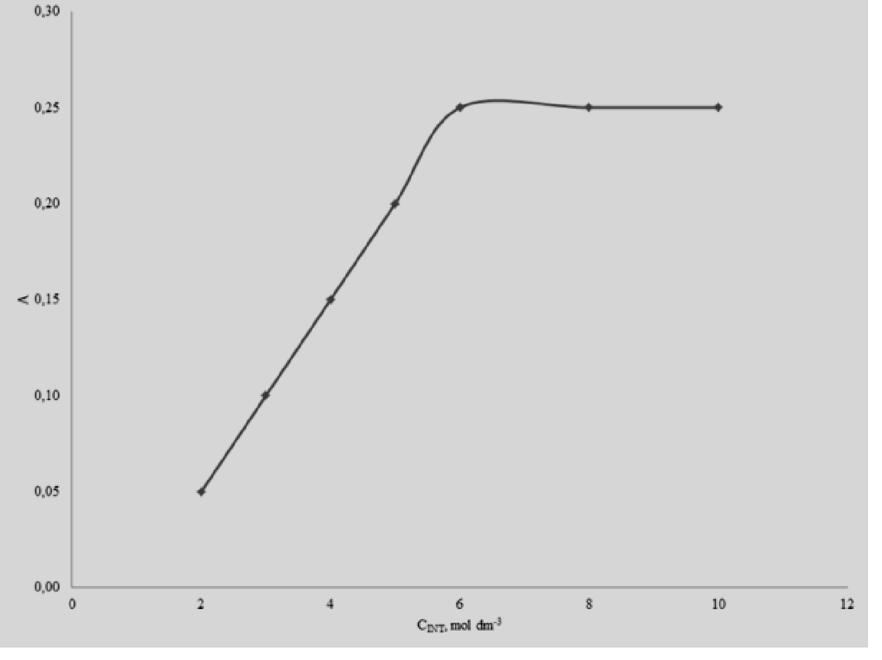

Fig. 7. Relationship between the change of associate light absorption and INT concentration:
$C_{Co(II)} = 1\times10^{-4}$ mol dm^{-3}, $C_{SCN} = 0.8$ mol dm^{-3}, b = 1 cm

An important factor in the photometric determination of cobalt is the tetrazolium salt. In order to maximize the recovery of the metal from the aqueous phase, the influence of different INT concentrations was investigated. The light absorption of the ion associate has a maximum value at a concentration of 6×10^{-4} mol dm^{-3} INT (Fig. 7). The figure shows that with increasing concentrations of the tetrazolium salt, light absorption of the associate remains constant.

Effect of Co(II) concentration on the light absorption

When INT was added to the thiocyanate solution of cobalt (II) pale green precipitate soluble in the organic solvent was obtained.

$INT + [Co(SCN)_4]^{2-} \rightarrow [INT]_2 [Co(SCN)_4]$

The intensity of the precipitate colour increased with increasing cobalt (II) concentration. Fig.8 displays that the relationship between cobalt (II) concentration and light absorption is linear in the range of 6 mg to 125 mg Co(II) in 10 ml aqueous phase.

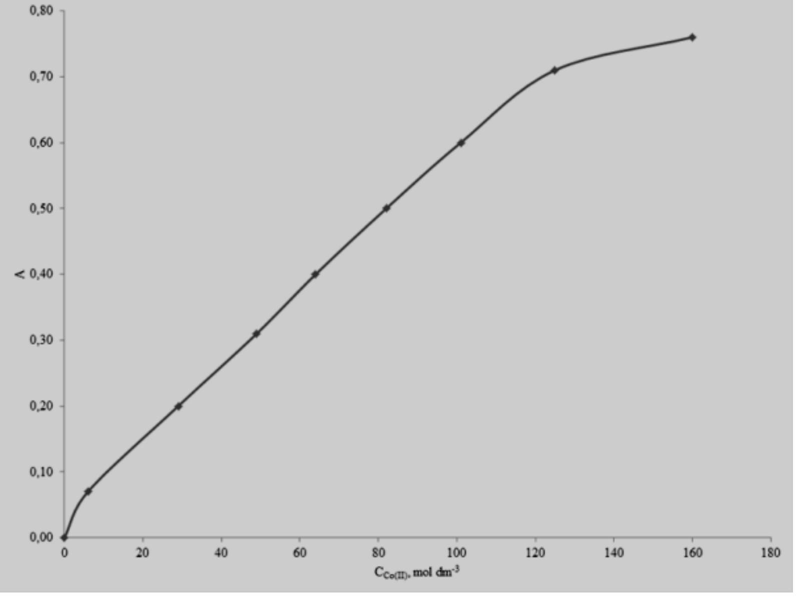

Fig. 8. Relationship between the change of light absorption and Co(II) concentration:
$C_{INT} = 10.5\times10^{-4}$ mol dm^{-3}, $C_{SCN} = 0.8$ mol dm^{-3}, b = 1 cm

Effect of side ions

To get a more complete picture of cobalt (II) extraction and to characterize the selectivity of the extraction, the influence of some ions, which would probably be contained in the analyzed samples, was studied. Experimental data are given in Table 2. The results qualify the tetrazolium salt used as a selective reagent for the determination of cobalt. Among all examined ions, only Fe (III) interferes the determination. The interference is removed by the addition of asc$_o$rbic acid as a masking agent. It has pronounced reduction properties.

Table 2. Effect of some ions on Co(II) extraction with INT: $C_{Co(II)} = 0.5\times10^{-4}$ mol dm^{-3}, $C_{INT} = 4.5\times10^{-4}$ mol dm^{-3}, $C_{SCN} = 0.8$ mol dm^{-3}

Side ion	Concentration limit of the side ion, mg	Limit ratio $C_x / C_{Co(II)}$, mg
K^+	300	10204:1
Na^+	100	3401:1
Sr^{2+};$S_2O_3^{2-}$	50	1700:1

$C_2O_4^{2-}$	20	680:1
Hg^{2+}	15	510:1
Al^{3+};Ca^{2+};Ni^{2+};BO_3^{3-}	10	340:1
Pb^{2+}	8	272:1
W^{6+}	7.4	251:1
Cd^{2+}	5	170:1
V^{5+}	0.5	17:1
Cr^{6+}	0.3	10:1
Br-	0.2	6.8:1
ЕДТА;NO_3-;J-;SO_4^{2-}	0.1	3.4:1
ClO_{4-}	0.05	1.7:1
Fe^{3+}	0.01	interfere

Application of the developed method for analysis of soil cobalt content

Accuracy and precision

Soil materials used for accuracy and precision tests include three certified soil samples corresponding to two main soil types in Bulgaria: (1) Light Alluvial–deluvial Meadow Soil PS-1, SOOMET No. 0001-1999 BG, SOD No. 310a-98; (2) Light Meadow Cinnamonic Soil PS-2, SOOMET No. 0002-1999 BG, SOD No.311a-98; (3) Light Alluvial–deluvial Meadow Soil PS-3, SOOMET No. 0003-1999 BG, SOD No. 312a-98.

For evaluation of the accuracy of the digestion and measuring procedures, we have used R criterion showing the extent of extraction of the element in percent from the certified value. When the measured value X is within the borders of $X_{CRM} \pm U_{CRM}$, where U_{CRM} is the indefiniteness of the certified value, we accept an extent of extraction to be 100%. In all the remaining cases, the extent of extraction is equal to $X / X_{CRM} \cdot 100$. As can be seen from the Table 1, the results obtained for all certified materials yield a recovery of 100% for Co.

Mineralization of the samples

The mineralization of the samples was carried out according to EPA Method 3052 procedure:[1)] 1g air - dry soil to the nearest 0.001 g in PTFE vessels was weighted. HNO_3, HF, HCl and H_2O_2, were added using a microwave system Multiwave 3000. The maximum power was 1400 W, and the maximum pressure in Teflon vessels - 40 bar.

Cobalt extraction

5 cm^3 soil samples, some drops of 1 mol dm^{-3} NaOH (for adjustment to pH 9.0-10.0) and 5 cm^3 0.02% dithizone in chloroform were consecutively placed in 100 cm^3 separating funnels. The systems were left to extract for 1min. Adequate quantity of HCl (1:1) (for adjustment of pH 1.0-2.0) and 2 cm^3 4 mol dm^{-3} thiocyanate solutions were added to the organic phase. Re-extraction for 1 min was accomplished. The organic phase was discharged, while 1 mol dm^{-3} NaOH (for pH 3.0-4.0), 0.6 cm^3 1.5×10^{-2} mol dm^{-3} INT and 2 cm^3 saturated solution of ascorbic acid (for masking of the interfering ions) were added to the aqueous phase. Distilled water was supplemented to a volume of 20 cm^3. Extraction with 3 cm^3 1,2-dichloroethane for 30 s was accomplished. After the stratification of both phases, the organic was filtered through a paper filter, placed in a cuvette, b = 1 cm, and photometered at λ = 630 nm.

A blank, not containing a soil sample, was also analyzed for reliability of the experimental results.

The experimental data are shown in Table 3. A good correlation of our results with data from included three certified soil samples was established.

Table 3. Determination of Co in soils

Element	Sample	Certified value	*INT* $X \pm \sigma$ mg kg^{-1}	*R*
Co	PS-1	11.42 ± 0.97	10.96 ± 0.023	96
	PS-2	10.56 ± 1.66	10.14± 0.019	96
	PS-3	12.5 ± 1.4	12.13± 0.036	97

Conclusions

The developed extraction spectrophotometric method for analysis of soil cobalt content with iodonitrotetrazolium chloride (INT) is simple, not expensive, express, characterized with selectivity and adequate acuracy.The good agreement of the results shows that INT can be used as a reagent for determination of microquantities of Co in soils and that pre-isolation of Co from most other ions is not necessary.

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NOTES

1. https://www.epa.gov/sites/production/files/2015-12/documents/3052.pdf

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